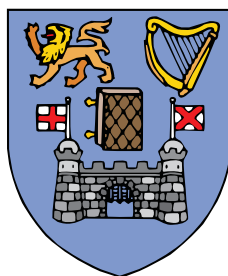


Near Electrode Effects in Magneto-Electrochemistry



Peter Dunne

School of Physics

Trinity College, University of Dublin

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Peter Dunne

Abstract

Magnetic fields imposed on electrochemical cells have been shown to have dramatic effects on electrodeposits ranging from surface morphology, crystal structure, deposition rate, alloy composition and magnetic properties. To further illuminate the effects of magnetic fields a number of electrochemical systems were studied ranging from metal deposition in uniform magnetic fields, organic liquid-liquid systems, and patterned metal deposits by permanent magnet arrays.

Lorentz force induced magneto-convection was observed to dominate during metal electrodeposition and corrosion, enhancing the mass transport of ions by thinning the diffusion layer. Using AC impedance methods the double layer and charge transfer kinetics were probed in a model one electron transfer system. The imposition of a magnetic field was observed to alter the structure of the double layer and the measured apparent kinetics of the system. No true magnetic shift in kinetics was observed, rather all the effects are due to the change in free energy at the interface due to the magnetostatic energy, which is manifested as an induced Maxwell stress and thus the increased attraction of ions to the electrode surface.

Patterned permanent magnet arrays were used to demonstrate magnetic templating using paramagnetic ions, inverse templating using rare-earth salts as contrast agents. The deposits were seen to follow the contours of $|\mathbf{B}|$, which can be explained in terms of the magnetostatic interaction developed in the model system. Magnetic templating is a potentially fruitful development that may scale below the micron dimensions demonstrated here.

In summary, all magnetic field effects in electrochemical systems can be described and understood through the determination of the energies involved. This avoids any erroneous derivation of forces from incorrect boundary condition assumptions, and can also take into account the magnetic stresses, or energies, which are ignored in a force model, where only net forces are considered.

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Chapter 1

Electrochemical Phenomena

1.1 Introduction

1.1.1 Electrochemical Cell

A standard three-electrode electrochemical cell consists of a working electrode (WE) where all the electrochemical measurements of interest are carried out, a counter electrode (CE) to supply current, and a reference electrode to measure the potential difference between it and the working electrode.

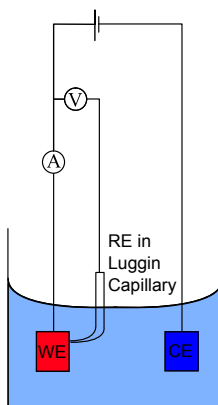


Figure 1.1: A three electrode electrochemical cell

1.1.2 Convention

There are two common, conflicting conventions used in electrochemical literature (see fig 1.2), the older American convention anodic (positive) potentials are plotted to the left of the origin, and cathodic currents are defined as positive. In the European convention, adopted by IUPAC, anodic (positive) potentials are plotted to the right of the origin, and anodic currents are positive. Only the IUPAC convention will be used.

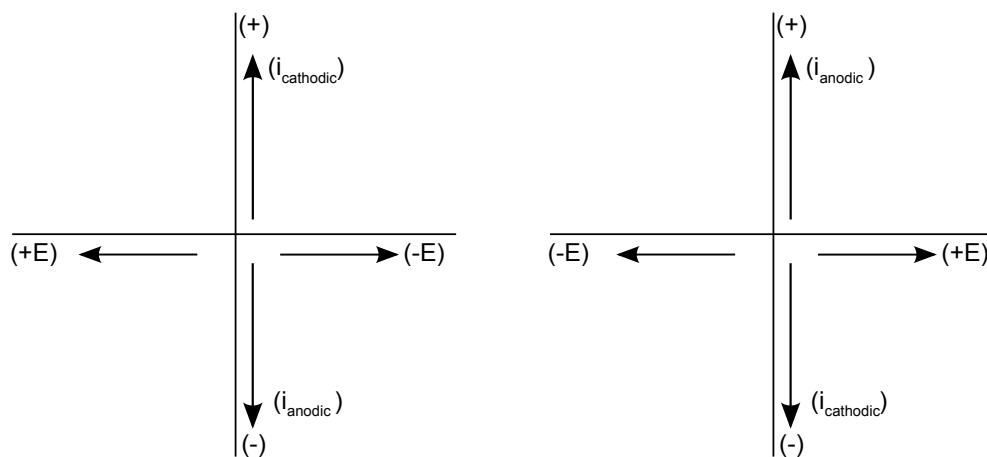


Figure 1.2: (a) American and (b) IUPAC voltammetry conventions

1.1.3 Cell Classification

Electrochemical cells are classified as either *galvanic cells* or *electrolytic cells*. Galvanic cells convert chemical energy into electrical energy via spontaneous homogeneous or heterogeneous reactions at the electrode surface. One example is a fuel cell, where hydrogen is oxidised at the anode (electrons are transferred to the anode), and oxygen is reduced at the cathode (receives electrons from the cathode). To sustain this process, electrons are transferred through an external electric circuit from the anode to the cathode, and the electric current can be used to power external devices.

Table 1.1: Comparison of Galvanic and Electrolytic Cells

Cell	Anode	Cathode
Galvanic	-	+
Electrolytic	+	-

An electrolytic cell in contrast requires an external electrical power source to drive chemical/electrochemical reactions. Taking the fuel cell example, in an electrolytic cell an external power source drives the reverse reaction which is the electrolysis of water. An electrolytic cell converts electrical energy to chemical energy and can be used as a form of energy storage such as rechargeable batteries. Other applications include extraction, refining and plating of metals (electrorefining, electrodeposition), electrolytic synthesis (e.g. chlorine), and brine electrolysis [1, 2].

1.2 Electrode Potentials

When an electrode is placed in an electrolyte solution, thermodynamic equilibrium is achieved between the electrode and the solution. In this situation reduction and

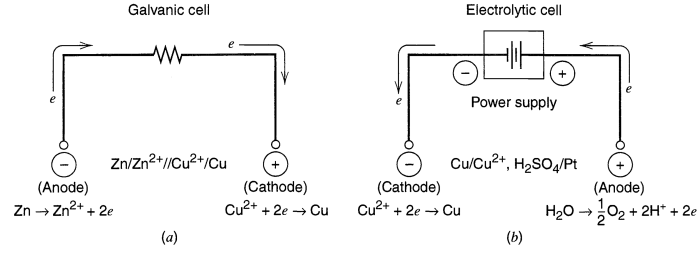


Figure 1.3: A comparison of a galvanic and electrolytic cells

oxidation reactions are balanced, and the interface is in dynamic equilibrium.



This equilibrium is characterised by the Nernst equation [1]

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{[\text{O}]_*}{[\text{R}]_*} \quad (1.2)$$

where $[\text{O}]_*$ and $[\text{R}]_*$ are the oxidised and reduced ion concentrations at the electrode surface, $E^{0'}$ is the *formal potential*, which is related to the *standard electrode potential* by

$$E^{0'} = E^0 + \frac{RT}{nF} \ln \frac{\gamma_{\text{O}}}{\gamma_{\text{R}}} \quad (1.3)$$

where γ_{O} and γ_{R} are the activity coefficients for the oxidised and reduced molecules. The important distinction to make between the standard and formal potentials is that the former is dependent on the ratio of *concentration*, while the latter is concerned with the ratio of *activity* of the oxidised and reduced forms of the species.

1.2.1 Reference Electrodes

Since an electrochemical system always has two electrode reactions associated with it, the reduction and oxidation processes, the standard electrode potential of a single process cannot be measured directly; only the potential difference can be measured. Therefore all potentials differences must be measured against a standard electrode reaction. The internationally accepted standard is the standard hydrogen electrode (SHE), or normal hydrogen electrode (NHE) [3].

1. ELECTROCHEMICAL PHENOMENA

1.2.1.1 Standard Hydrogen Electrode

The standard hydrogen electrode reaction is



and its standard potential is formally defined as $E^0 = 0\text{V}$ at all temperatures [4], noting that this is not the absolute scale, where the potential obeys Arrhenius' law. The standard hydrogen electrode can be used as in fig. 1.4, the schematic is described

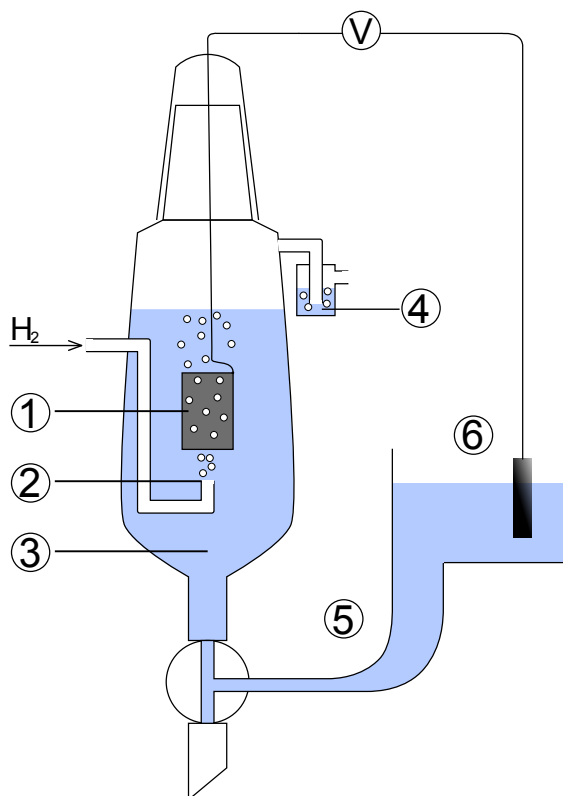


Figure 1.4: Example use of standard hydrogen electrode. Refer to text for key.

as

1. Platinised platinum electrode
2. Hydrogen gas source
3. Solution, with activity of $\gamma_{\text{H}^+} = 1\text{ mol l}^{-1}$
4. Hydroseal to prevent oxygen contamination
5. Salt bridge
6. Working electrode where the measured redox reaction occurs

Hydrogen electrodes are cumbersome to use in the laboratory, so typically mercury calomel or silver-silver chloride reference electrodes are used in practise. Table 1.4 lists conversion offsets for some common reference electrodes in aqueous solutions.

The two most relevant reference electrodes are the silver-silver chloride electrode, and the silver-silver cation reference electrode.

1.2.1.2 Silver/silver chloride (Ag/AgCl)

The silver-silver chloride reference electrode is the most commonly used RE due to its simplicity, inexpensive design, and nontoxic components [5]. Redox reaction:



1.2.1.3 Silver/Silver cation (Ag/Ag⁺)

Silver-silver cation reference electrode are mostly used in non-aqueous solutions, with AgNO₃ and the supporting electrolyte of the solution of interest are in the RE compartment. The reference potential is influenced by the choice of solution, and must be calibrated if a standard scale is to be used. In acetonitrile with 10 mM AgNO₃ the potential is 0.3 V versus SCE_{ag} [6].

Redox reaction:

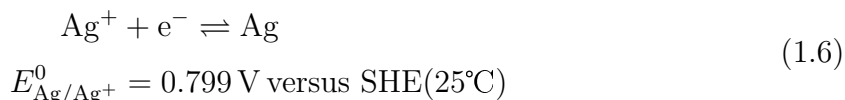


Table 1.2: Estimated Standard Potentials in Aprotic Solvents vs. aq SCE [1].

Substance	Reaction	Conditions	Potential vs. aq SCE V
Anthracene (An)	$\text{An} + \text{e}^- \rightleftharpoons \text{An}^{\bullet-}$	DMF, 0.1M TBAI	-1.92
	$\text{An}^{\bullet-} + \text{e}^- \rightleftharpoons \text{An}^{2-}$	DMF, 0.1M TBAI	-2.5
	$\text{An}^{\bullet+} + \text{e}^- \rightleftharpoons \text{An}$	MeCN, 0.1M TBAP	1.3
Ferrocene (Cp ₂ Fe)	$\text{Cp}_2\text{Fe}^+ + \text{e}^- \rightleftharpoons \text{Cp}_2\text{Fe}$	MeCN, 0.2M LiClO ₄	0.31
Nitrobenzene (NB)	$\text{NB} + \text{e}^- \rightleftharpoons \text{NB}^{\bullet-}$	MeCN, 0.1M TEAP	-1.15
Oxygen	$\text{O}_2 + \text{e}^- \rightleftharpoons \text{O}^{\bullet 2-}$	DMF, 0.2M TBAP	-0.87
	$\text{O}_2 + \text{e}^- \rightleftharpoons \text{O}^{\bullet 2-}$	MeCN, 0.2M TBAP	-0.82
	$\text{O}_2 + \text{e}^- \rightleftharpoons \text{O}^{\bullet 2-}$	DMSO, 0.1M TBAP	-0.73

1. ELECTROCHEMICAL PHENOMENA

Table 1.3: Selected standard electrode potentials in aqueous solutions at 25°C vs. SHE [1].

Reaction	Potential vs. SHE V
$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$	+0.7991
$\text{Au}^+ + \text{e}^- \rightleftharpoons \text{Au}$	+1.83
$\text{Au}^{3+} + 2\text{e}^- \rightleftharpoons \text{Au}$	+1.36
$\text{Co}^{2+} + 2\text{e}^- \rightleftharpoons \text{Co}$	-0.277
$\text{Co}^{3+} + \text{e}^- \rightleftharpoons \text{Co}^{2+}$	+1.92
$\text{HClO} + \text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2}\text{Cl}_2 + \text{H}_2\text{O}$	+1.63
$\text{Cu}^+ + \text{e}^- \rightleftharpoons \text{Cu}$	+0.520
$\text{Cu}^{2+} + \text{e}^- \rightleftharpoons \text{Cu}^+$	+0.159
$\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}$	+0.340
$\text{Fe}^{2+} + 2\text{e}^- \rightleftharpoons \text{Fe}$	-0.44
$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	+0.771
$\text{Fe}(\text{CN})_6^{3-} + \text{e}^- \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}$	+0.3610
$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$	0.000
$2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{H}_2 + 2\text{OH}^-$	-0.828
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	+1.763
$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}_2$	+0.695
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	+1.229
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightleftharpoons 4\text{OH}^-$	+0.401
$\text{O}_3 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{O}_2 + \text{H}_2\text{O}$	+2.075
$\text{Pt}_2 + 2\text{e}^- \rightleftharpoons 2\text{Pt}$	+1.188

Table 1.4: Aqueous RE potential scale conversions [5].

Electrode description		Hydrogen	Mercury					Silver chloride	
			Calomel			Sulfate	Oxide		
To convert	From To	NHE or SHE	SCE	SSCE	NCE	MSRE	1M NaOH	Saturated KCl/NaCl	3M KCl/NaCl
Hydrogen	NHE or SHE	0	-0.241	-0.236	-0.280	-0.640	-0.098	-0.197	-0.209
Mercury	Calomel	SCE	+0.241	0	+0.005	-0.039	-0.399	+0.143	+0.044
		SSCE	+0.236	-0.005	0	-0.044	-0.404	+0.138	+0.039
		NCE	+0.280	+0.039	+0.044	0	-0.360	+0.182	+0.083
	Sulfate	MSRE	+0.640	+0.399	+0.404	+0.360	0	+0.542	+0.443
	Oxide	1M NaOH	+0.098	-0.143	-0.138	-0.182	-0.542	0	-0.099
Silver chloride	Saturated KCl/NaCl		+0.197	-0.044	-0.039	-0.083	-0.443	+0.099	0
	3M KCl/NaCl		+0.209	-0.032	-0.027	-0.071	-0.443	+0.111	+0.012

1. ELECTROCHEMICAL PHENOMENA

1.2.1.4 iR Compensation

The position of the reference electrode is also critical for potential measurements. A small but finite current flows through the reference electrode, which lies somewhere in solution between the working and counter electrodes. In effect, most but not all of the cell resistance is eliminated, there is still a small iR drop from the uncompensated cell resistance (fig. 1.5). Hence in any measurement in electrochemistry it is important to carry out iR compensation.

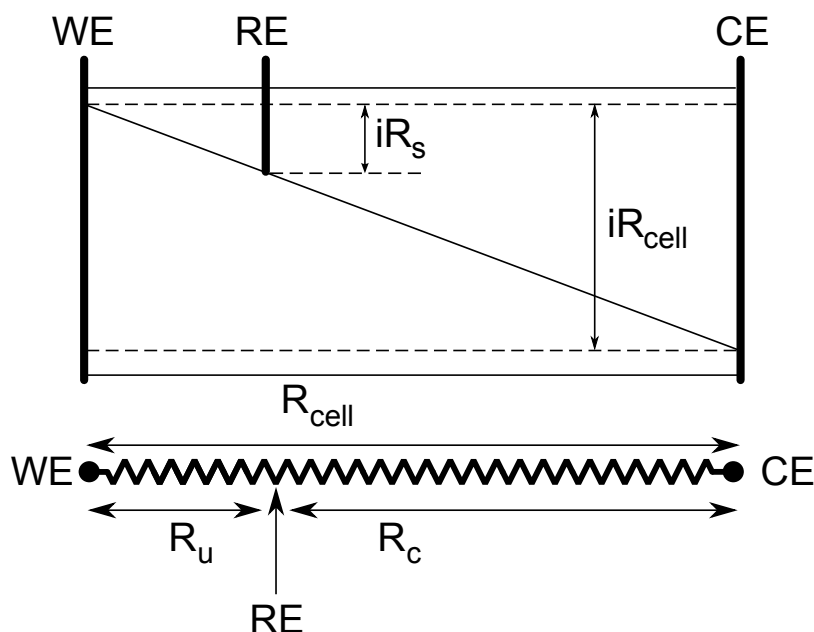


Figure 1.5: Schematic of the uncompensated solution iR drop between the working electrode and reference electrode.

The three main approaches to dealing with the solution iR drop are (i) measure the cell resistance with impedance spectroscopy (§1.6.3) followed by post-processing of the data, (ii) the current interrupt method, and (iii) the positive feedback method.

In the second approach the current is interrupted briefly, there is a voltage drop $V_{iR} = iR$, followed by a much slower decay of the voltage due to the slower discharge of the faradaic capacitance. A fine balance must be kept between interrupting for too long a time, allowing the faradaic response to decay, and not long enough to allow all the uncompensated resistance to drop across the electrode.

The third approach is to use op-amps to introduce positive feedback between the working electrode and the potentiostat. An extra resistance R_c is added between the working electrode and potentiostat to match the cell resistance. When $R_c > R_{cell}$ positive feedback will cause the potentiostat to oscillate. The resistance is then decreased to a value on the threshold of oscillation.

1.3 Electrode Kinetics

Even for simple one-electron transfer reactions, the mechanisms are complicated, requiring classical and quantum mechanical approaches [7–14] (see [15] for a rigorous description of electron transfer including second order effects). A simple description of the steps involved, with the characteristic timescales are as follows [2] (see fig. 1.6).

1. Diffusion of the ion to the electrode surface (see § 1.5.1).
2. Rearrangement of the ionic atmosphere (10^{-8} s).
3. Reorientation of the solvent dipoles (10^{-11} s)
4. Alterations in the distances between the central ion and the ligands (10^{-14} s).
5. Electron transfer (10^{-16} s).
6. Relaxation (the inverse of steps 4-1).

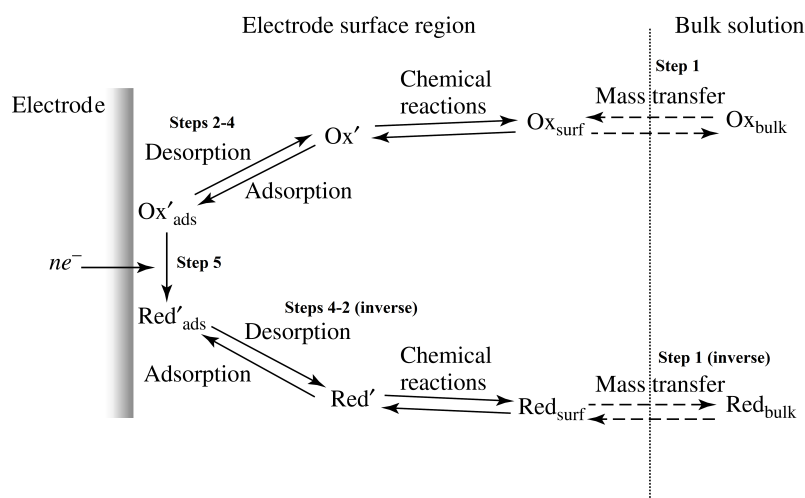


Figure 1.6: Simple schematic of electron transfer at an electrode [2].

1.3.1 The Butler-Volmer Equation

For any electrode reaction, Arrhenius' relation states that the natural logarithm of the kinetic rate constant is proportional to the standard free energy of activation, and inverse temperature [16].

$$k = A \exp [-E_A/RT] \quad (1.7)$$

1. ELECTROCHEMICAL PHENOMENA

From (1.7) we obtain the following expressions for the oxidation and reduction reaction rates

$$k_a = k_0 \exp \left[\frac{\alpha_a n F}{RT} (E - E^{0'}) \right] \quad (1.8a)$$

$$k_c = k_0 \exp \left[-\frac{\alpha_c n F}{RT} (E - E^{0'}) \right] \quad (1.8b)$$

where k_0 is the standard rate constant at equilibrium, and α_a , α_c are the charge transfer coefficients of the oxidation and reduction steps respectively. For a simple reversible one electron transfer system α_a is also defined as $\alpha_a = 1 - \alpha_c$

The charge transfer coefficient, α , was originally introduced by Erdey-Gruz and Volmer [17] for the hydrogen evolution reaction (HER). It is a measure of the symmetry of the activation barriers for the oxidation and reduction reactions, and can take on values from 0 to 1. $\alpha = 0.5$ corresponds to a symmetric barrier with both activated complexes equally likely; $\alpha = 0$ corresponds to the oxidised species and $\alpha = 1$ to the reduced species being the predominant species in solution (see fig. 1.7).

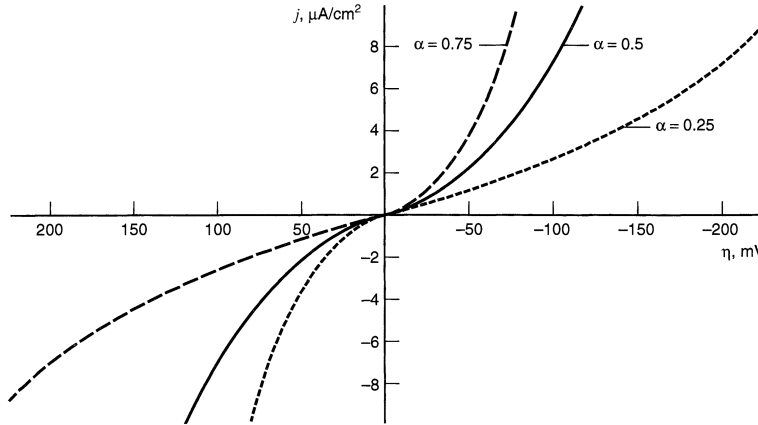


Figure 1.7: Effect of the transfer coefficient on the symmetry of an IV curve for a simple redox reaction [1]. NB: the American convention is used in this plot.

Butler and Volmer observed that the measured current for kinetic control is proportional to the difference between the rate of the oxidation and reduction reactions at the electrode surface and is given by [17, 18]

$$i = nFA(k_a[R]_* - k_c[O]_*) \quad (1.9)$$

At equilibrium (when the overpotential $\eta = (E - E^{0'}) = 0$) there is no *net* current, but there are two *exchange currents*, corresponding to the oxidation and reduction steps at the electrode, when $[O]_\infty \neq [R]_\infty$ the exchange current is

$$i_0 = nFAk_0[O]_\infty^{1-\alpha_c}[R]_\infty^{\alpha_c} \quad (1.10)$$

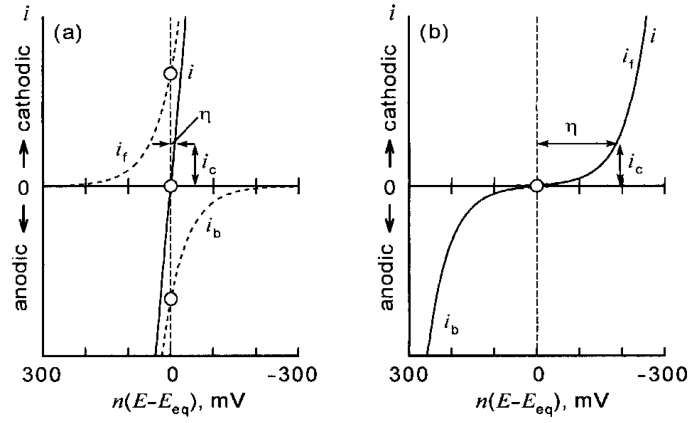


Figure 1.8: I-V curves for for electrode reactions with (a) a large exchange current (small overpotential activation) and (b) a small exchange current (large overpotential activation). [19]. NB: the American convention is used in this plot.

For a first order reaction, the rate constant is proportional to the concentration of one of the reactants, and independent of all other concentrations. The rate constant of a first order reaction at equilibrium are related by

$$k_c[O]_* = k_a[R]_* \quad (1.11)$$

and so when $[O]_* = [R]_\infty = c_\infty$ the exchange current becomes

$$i_0 = nFAk_0c_\infty \quad (1.12)$$

Substituting (1.8a), (1.8b) and (1.10) into (1.9)

$$i = i_0 \left[\frac{[O]_*}{[O]_\infty} \exp\left(-\frac{\alpha_c n F \eta}{RT}\right) - \frac{[R]_*}{[R]_\infty} \exp\left(\frac{\alpha_a n F \eta}{RT}\right) \right] \quad (1.13)$$

When the surface concentrations of oxidised and reduced species do not deviate much from the bulk solution concentrations, i.e. at low potential and under well defined hydrodynamic conditions (e.g. stirred solutions), (1.13) reduces to the Butler-Volmer equation

$$i = i_0 \left[\exp\left(-\frac{\alpha_c n F \eta}{RT}\right) - \exp\left(\frac{\alpha_a n F \eta}{RT}\right) \right] \quad (1.14)$$

The Butler-Volmer equation only deals with the kinetics of the system at the electrode surface. It tells us that on changing the potential we can change the kinetic rate constants k_a and k_c exponentially. It does not, however, deal in any way with a mass-transport limited system (§1.5). Instead it assumes that the reacting ions are supplied to the electrode surface faster than they can be consumed. When a large overpotential is applied this is no longer the case, the applied rate of reaction is faster than the rate that the ions arrive to the surface.

1. ELECTROCHEMICAL PHENOMENA

The two limiting cases for a kinetically controlled system are

(i) Low overpotential limit, polarisation resistance

$$i = i_0 \frac{\alpha_c n F \eta}{RT} \quad (1.15)$$

(ii) High overpotential limit, Tafel law

$$\log i = \log i_0 - \alpha_c \left(\frac{nF\eta}{RT} \right) \text{ cathodic reaction} \quad (1.16a)$$

$$\log i = \log i_0 + \alpha_a \left(\frac{nF\eta}{RT} \right) \text{ anodic reaction} \quad (1.16b)$$

Equations 1.16a and 1.16b can be recast in the form most familiar to electrochemists as that defined by Tafel in 1905 [20]

$$\eta = a + b \log i \quad (1.17)$$

Plots of $\log |i|$ versus η are known as *Tafel plots*, and it is possible to extract α from the cathodic slope $a (= -\alpha n F / 2.3 RT)$ or anodic slope $a (= \alpha n F / 2.3 RT)$, and $b = \log i_0$.

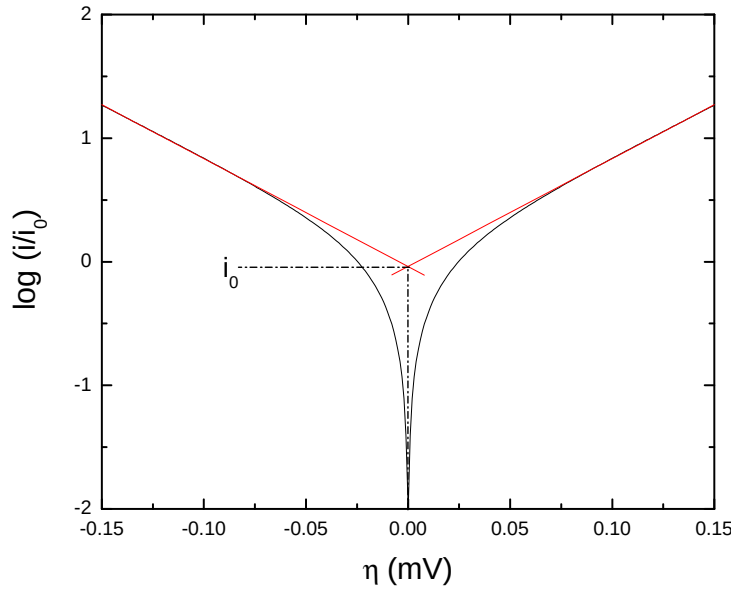


Figure 1.9: A typical Tafel plot calculated from (1.14).

1.3.2 Microscopic Model

It is useful to distinguish between two kinds of electron transfer reactions at electrode surfaces, names *inner-sphere* and *outer-sphere* electron-reactions (fig. 1.10) The term “outer-sphere” denotes a reaction where chemical bonds are neither formed nor broken.

During such a reaction, the charge on the reactant, and hence the configuration of its solvation sheath, changes.

The order in which electron transfer and solvent reorganization occur is governed by the Frank-Condon principle which is an adiabatic process where all atoms and ligands are frozen into place during electron transfer [21], i.e. the nuclear momenta and positions do not change on the time scale of electronic transitions. Obviously, it would be energetically unfavourable if electron

transfer were to take place before the solvent had started to reorganize, since the reactant would be surrounded, and inhibited by a solvation sheath with different charge. Likewise, a solvent reorganization prior to electron transfer would require high energy, and is equally unlikely. Therefore, the solvation sheath must first take up a configuration between those for the initial and the final charge state, then the electron is transferred, and the system relaxes. In an “inner-sphere” reaction there is a strong interaction between the reactant, intermediates or products and the electrode; such as specific adsorption of the ion, or a specifically adsorbed ion that acts as a ligand bridge between an ion and electrode surface. Likewise, in an outer-sphere electrode reaction, the reactant and product do not interact strongly with the electrode surface, and they are generally at a distance of at least a solvent layer from the electrode. Some notable examples include the reduction of $\text{Ru}(\text{NH}_3)_3^{3+}$ which is an outer-sphere reaction, compared to the reduction of oxygen in water and the oxidation of hydrogen at Pt which are inner-sphere reactions [1]. Finally, outer-sphere reactions are less dependent on electrode material than inner-sphere ones. [22].

One-electron transfer reactions in aromatic compounds such as nitrobenzene and anthracene and of the type



are outer-sphere reactions [19]. Generally $\text{Q}^{\bullet-}$ is reactive, but if it has a delocalised negative charge it has a reasonably long lifetime in aprotic solvents with tetraalkylammonium salt supporting electrolytes. These type of redox reactions are generally reversible as Q and $\text{Q}^{\bullet-}$ have similar structures and sizes.

For an adiabatic outer-sphere reaction, the standard rate constant, k_0 can, according to the Marcus model, be expressed as [19]

$$k_0 = \kappa K_p \nu_n \exp\left(\frac{-\Delta G^*}{RT}\right); \nu_n = \tau_L^{-1} \sqrt{\frac{\Delta G^*}{4\pi RT}} \quad (1.19)$$

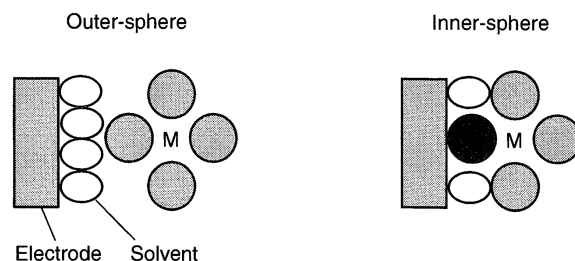


Figure 1.10: Outer-sphere and inner-sphere reactions.

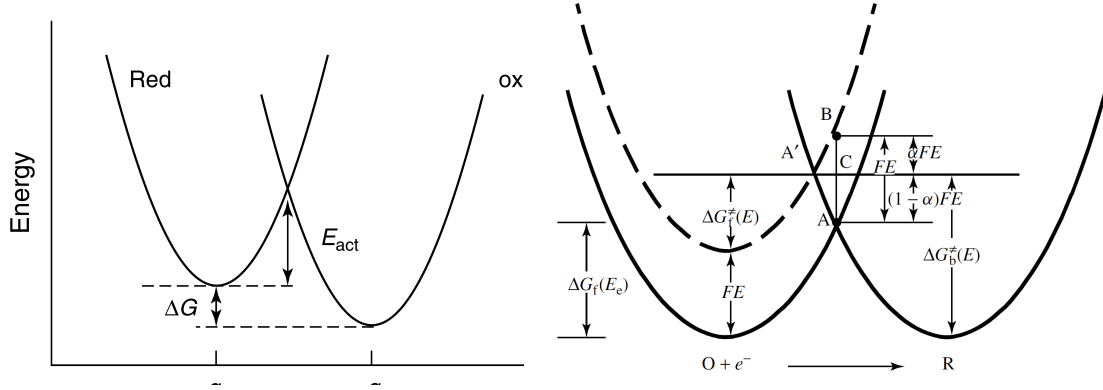


Figure 1.11: (a) Potential energy vs. generalized solvent coordinate q in Marcus theory [21] and (b) the effect of electrode potential on the free energy versus reaction coordinate curves for an electron reactant at two electrode potentials: $\eta = 0$ (solid line) and $\eta < 0$ (broken line) [19].

where κ is the electron transmission coefficient (≈ 1), K_p is the pre-equilibrium constant, ν_n is the nuclear frequency factor (in s^{-1}), which represents the frequency of attempts on the barrier, τ_L^{-1} is the longitudinal solvent relaxation time, ΔG^* is the activation energy $\Delta G^* = \Delta G_{is}^* + \Delta G_{os}^*$. ΔG_{is}^* is the inner-shell activation energy due to the reorganization of reactant itself, ΔG_{os}^* is the outer-shell activation energy due to the reorganization of the solvent around the reactant. Here it is assumed that $\Delta G_{os}^* \gg \Delta G_{is}^*$. By using the Born model, ΔG_{os}^* can be expressed by

$$\Delta G_{os}^* = \frac{N_A e^2}{32\pi\epsilon_0} \left(\frac{1}{r} - \frac{1}{2R} \right) \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \quad (1.20)$$

where r is the radius of the reactant, $2R$ is the distance between the reactant and its image charge in the electrode, ϵ_{op} and ϵ_s are the optical and static permittivities, and $\epsilon_{op}^{-1} - \epsilon_s^{-1}$ is known as the solvent Pekar factor.

1.4 Interfacial Region

In the previous section electrode kinetics were discussed without consideration of the nature of the interface where the reactions take place. The thermodynamics of the system, and the kinetics can be strongly influenced by the structure of the interfacial region. Here the solution-side region, referred to as the *double layer* will be discussed.

1.4.1 Double Layer Models

To first approximation, any excess charge on a metallic electrode, on the solution-side resides, only at the surface¹. The two primary methods of measuring the double

¹see [1, §3.5] for a discussion of the Jellium model

layer capacitance are impedance spectroscopy (§ 1.6.3) and electrocapillary curves (see [1, 2].)

1.4.1.1 Helmholtz Model

In 1879 Helmholtz considered a single rigid layer of counter ions from solution balanced against the excess charge on the electrode surface.

Helmholtz's treatment is essentially a parallel plate capacitor, and it is from Helmholtz's writings that we use the term *double layer* [23–25]. The stored charge density σ for a voltage drop V across a parallel plates capacitor is

$$\sigma = \frac{\epsilon\epsilon_0 A}{d} V \quad (1.21)$$

The differential capacitance is therefore

$$\begin{aligned} \frac{\partial\sigma}{\partial V} = C_d &= \frac{\epsilon\epsilon_0 A}{d} \\ &= \frac{\epsilon\epsilon_0 A}{x_H} \end{aligned} \quad (1.22)$$

where x_H is the closest approach of the ions to the electrode surface, which was assumed to be the ionic radius even though in effect the ions are treated as point charges. In Helmholtz's model the differential capacitance is independent of applied voltage. Comparing this to experimental data (fig. 1.16) we can see the weakness of such a model. Helmholtz's model fails to take into account any variation of electrode charge with applied voltage.

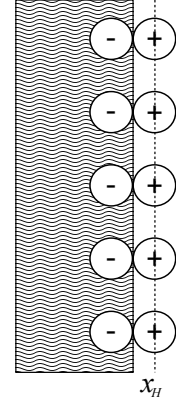


Figure 1.12: Schematic of Helmholtz's simple compact double layer model.

1.4.1.2 Gouy-Chapman Model

To improve upon the deficiencies of Helmholtz's model Gouy [26] and Chapman [27] independently derived a diffuse double layer model that took into account the applied potential and electrolyte concentration. In their model, the electric profile is described by the Poisson equation which relates the potential ϕ with the charge distribution $\rho(x)$

$$\frac{\partial^2 \phi_\Delta}{\partial x^2} = -\frac{\rho(x)}{\epsilon_r \epsilon_0} \quad (1.23)$$

and Boltzmann's law determines the distribution of ions

$$n_i = n_i^0 \exp \left[\frac{-z_i e \phi_\Delta}{k_B T} \right] \quad (1.24)$$

where $\phi_\Delta = \phi - \phi_s$, z_i the ion charge and n_i^0 is the number concentration of ions i in bulk solution.

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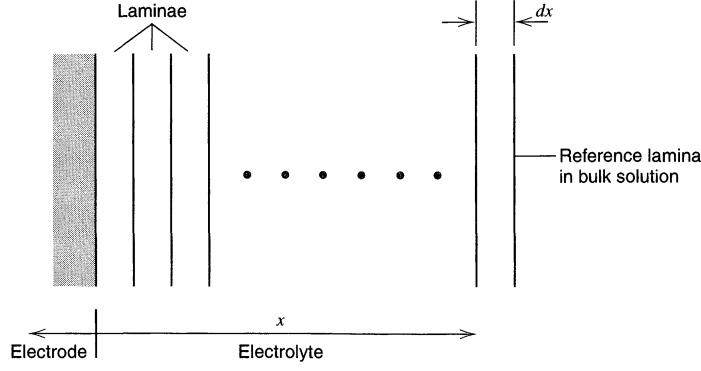


Figure 1.13: View of the solution near the electrode surface as a series of laminae [1].

Their approach was to divide the solution into laminae (see fig 1.13), so that the total charge density is

$$\begin{aligned}\rho(x) &= \sum_i n_i z_i e \\ &= \sum_i n_i^0 z_i e \exp \left[\frac{-z_i e \phi_\Delta}{k_B T} \right]\end{aligned}\tag{1.25}$$

arriving at the Poisson-Boltzmann equation

$$\frac{\partial^2 \phi_\Delta}{\partial x^2} = -\frac{e}{\epsilon_r \epsilon_0} \sum_i n_i^0 z_i e \exp \left(\frac{-z_i e \phi_\Delta}{k_B T} \right)\tag{1.26}$$

Remembering that

$$\frac{\partial^2 \phi_\Delta(x)}{\partial x^2} = \frac{1}{2} \frac{\partial}{\partial \phi_\Delta} \left(\frac{\partial \phi_\Delta}{\partial x} \right)^2\tag{1.27}$$

we arrive at

$$\left(\frac{\partial \phi_\Delta}{\partial x} \right)^2 = -\frac{2e}{\epsilon_r \epsilon_0} \sum_i n_i^0 z_i e \exp \left(\frac{-z_i e \phi_\Delta}{k_B T} \right) d\phi\tag{1.28}$$

Integration with the following boundary conditions gives

$$x = 0, \quad \phi_\Delta = \phi_{\Delta,0}\tag{1.29a}$$

$$x \rightarrow \infty, \quad \phi_\Delta \rightarrow 0 \quad (\delta \phi_\Delta / \delta x) = 0\tag{1.29b}$$

$$\left(\frac{\partial \phi_\Delta}{\partial x} \right)^2 = \frac{2k_B T}{\epsilon_r \epsilon_0} \sum_i n_i^0 \left[\exp \left(\frac{-z_i e \phi_\Delta}{k_B T} \right) - 1 \right]\tag{1.30}$$

Which simplifies for a symmetric $z : z$ electrolyte (one which has only one cation and anion, both of charge z) to

$$\frac{\partial \phi_\Delta}{\partial x} = \left(\frac{8k_B T n_i^0}{\epsilon_r \epsilon_0} \right)^{1/2} \sinh \left(\frac{ze \phi_\Delta}{2k_B T} \right)\tag{1.31}$$

Integrating a rearranged form

$$\int_{\phi_{\Delta,0}}^{\phi_{\Delta}} \frac{d\phi_{\Delta}}{\sinh(ze\phi_{\Delta}/2k_B T)} = - \left(\frac{8k_B T n_i^0}{\epsilon_r \epsilon_0} \right)^{1/2} \int_0^x dx \quad (1.32)$$

leads to

$$\frac{2k_B T}{ze} \ln \left[\frac{\tanh(ze\phi_{\Delta}/4k_B T)}{\tanh(ze\phi_{\Delta,0}/4k_B T)} \right] = - \left(\frac{8k_B T n_i^0}{\epsilon_r \epsilon_0} \right)^{1/2} x \quad (1.33)$$

or

$$\left[\frac{\tanh(ze\phi_{\Delta}/4k_B T)}{\tanh(ze\phi_{\Delta,0}/4k_B T)} \right] = \exp[-x/x_{DL}] \quad (1.34)$$

where x_{DL} , or κ^{-1} is the characteristic thickness of the diffuse double layer, i.e. its Debye length.

$$x_{DL} = \left(\frac{\epsilon_r \epsilon_0 k_B T}{2n_i^0 z^2 e^2} \right)^{1/2} \quad (1.35)$$

This characteristic thickness is much smaller than that encountered in the diffusion layer (see §1.5.1.1, c.f. table 1.5), for an aqueous solution at 298 K ($\epsilon_r = 78$) for an ion with $c_{\infty} = 1 \text{ mol l}^{-1}$ and $z = 1$, $x_{DL} = 0.3 \text{ nm}$. The diffuse layer capacitance can be

Table 1.5: Characteristic thickness of the diffuse layer calculated from (1.35).

c_{∞} (mol l^{-1})	x_{DL} or κ^{-1} (nm)
1	0.30
10^{-1}	0.96
10^{-2}	3.04
10^{-3}	9.62
10^{-4}	30.4

derived from (1.31) since the charge density is

$$\begin{aligned} \sigma_M &= \epsilon_r \epsilon_0 \left(\frac{\partial \phi_{\Delta}}{\partial x} \right)_{x=0} \\ &= (8k_B T \epsilon_r \epsilon_0 n_i^0)^{1/2} \sinh \left(\frac{ze\phi_{\Delta,0}}{2k_B T} \right) \end{aligned} \quad (1.36)$$

which when differentiated gives

$$C_{d,GC} = \frac{\partial \sigma_M}{\partial \phi_{\Delta,0}} = \left(\frac{2z^2 e^2 \epsilon_r \epsilon_0 n_i^0}{k_B T} \right) \cosh \left(\frac{ze\phi_{\Delta,0}}{2k_B T} \right) \quad (1.37)$$

The cosh term in Gouy and Chapman's model exhibits a dependence of capacitance on applied potential (see fig. 1.14), with a minimum at E_{pzc} , which is the point of zero charge on the surface at a specific potential. For potentials close to E_{pzc} this model can accurately describe the process, or at low concentrations. At large potentials the

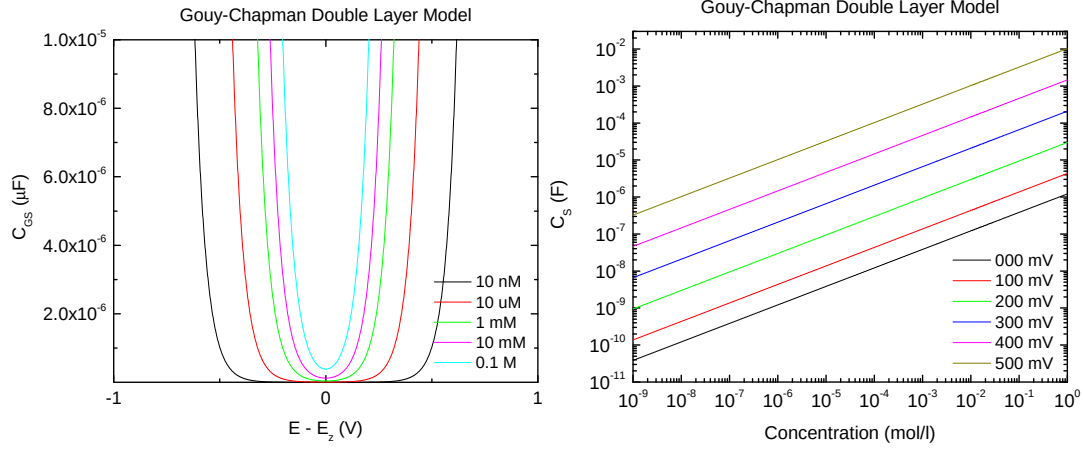


Figure 1.14: (a) Capacitance-Voltage curves for different ion concentrations and (b) capacitance-concentration curves for different voltages; calculated from the Gouy-Chapman double layer model (equation (1.37)).

capacitance rises rapidly to unphysical values as ions are treated as point charges, hence there is no maximum concentration of ions at the surface.

1.4.1.3 Stern Model

To overcome the limitations in both previous models, in 1924 Stern combined Helmholtz's model for values far from E_{pzc} and Gouy-Chapman theory for values close to E_{pzc} [28]. In essence he considered the double layer to consist of two sub-layers. The first layer, compact layer or Outer Helmholtz Plane (OHP), close to the electrode he treated as a parallel plate capacitor, followed by a diffuse double layer extending into the bulk solution [2]. Mathematically, this can be described as two capacitors in series

$$\begin{aligned} \frac{1}{C_S} &= \frac{1}{C_H} + \frac{1}{C_{GC}} \\ &= \frac{x_H}{\epsilon_r \epsilon_0} + \frac{1}{(2\epsilon_r \epsilon_0 z^2 e^2 n_i^0 / k_B T)^{1/2} \cosh(ze\phi_{\Delta,0}/2k_B T)} \end{aligned} \quad (1.38)$$

where C_H is the Helmholtz capacitance, and C_{GC} is the Gouy-Chapman capacitance. For two capacitors in series, the smaller of the two capacitors is the dominant term, at potentials far from E_{pzc} the ions are tightly bound to the electrode surface. All the potential drop is across the compact layer, and the diffuse layer is then a negligible contribution to the total capacitance. This was the most accurate model so far to describe the double layer capacitance behaviour with applied potential. A cursory comparison of figures 1.15 and 1.16 (b) reveal that the Stern model captures most, but not all of double layer structure.

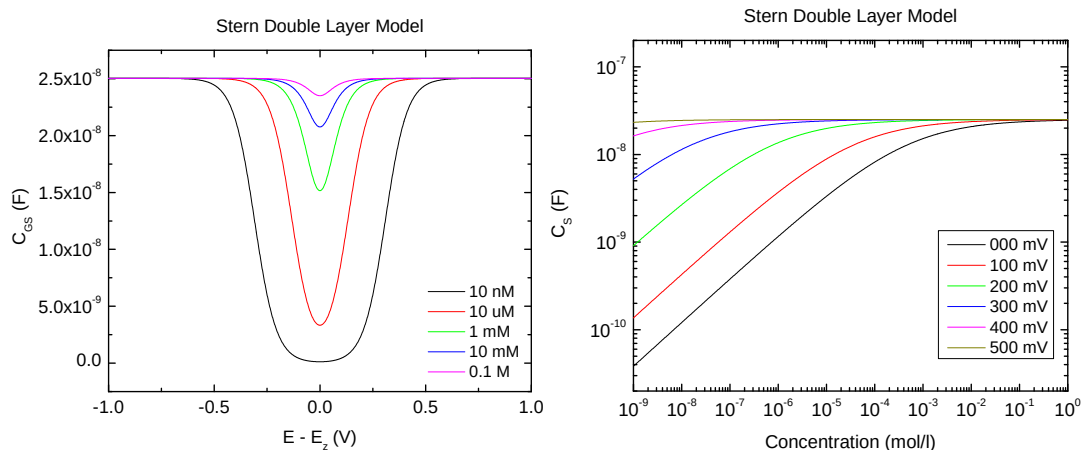


Figure 1.15: (a) Capacitance-Voltage curves for different ion concentrations and (b) capacitance-concentration curves for different voltages; calculated from the Stern double layer model (equation (1.38)).

1.4.1.4 Grahame Model

While Stern's model distinguished between ions adsorbed on the electrode surface and those in the diffuse layer, Grahame developed this further [29], including a second compact layer due to specific adsorption (see §1.4.4). In contrast to a non-specifically adsorbed ion, a specifically adsorbed ion loses its solvation sphere on the electrode surface, and its charge can be the same sign or the opposite sign to the electrode charge. These specifically adsorbed ions are tightly bound to the electrode surface and form a plane of charge, called the Inner Helmholtz Plane (IHP), closer to the electrode surface than the OHP. At potentials close to E_{pzc} it is possible to detect the influence of neutral adsorbates. The rationale being that a neutral molecule must displace a solvent molecule or electrolyte ion from the electrode surface; which can only occur at low potentials. At higher potentials the ions are tightly bound to the electrode surface making it energetically unfavourable for a neutral ion to specifically adsorb. The strength of Grahame's model is that it is semi-empirical in nature [30]. Grahame postulated that the compact Helmholtz layer capacitance is independent of ion concentration in the diffuse layer, but avoids any model hypothesis for the dependence of C_H on the electrode charge σ . In this fashion the diffuse layer behaviour is fully known, and $C_H(\sigma)$ is determined from experimental measurements.

1.4.2 Surface Roughness

So far only smooth surfaces have been considered; very rough electrodes can be modelled as fractals [31], but have been done so with little success [32]. In the limit of

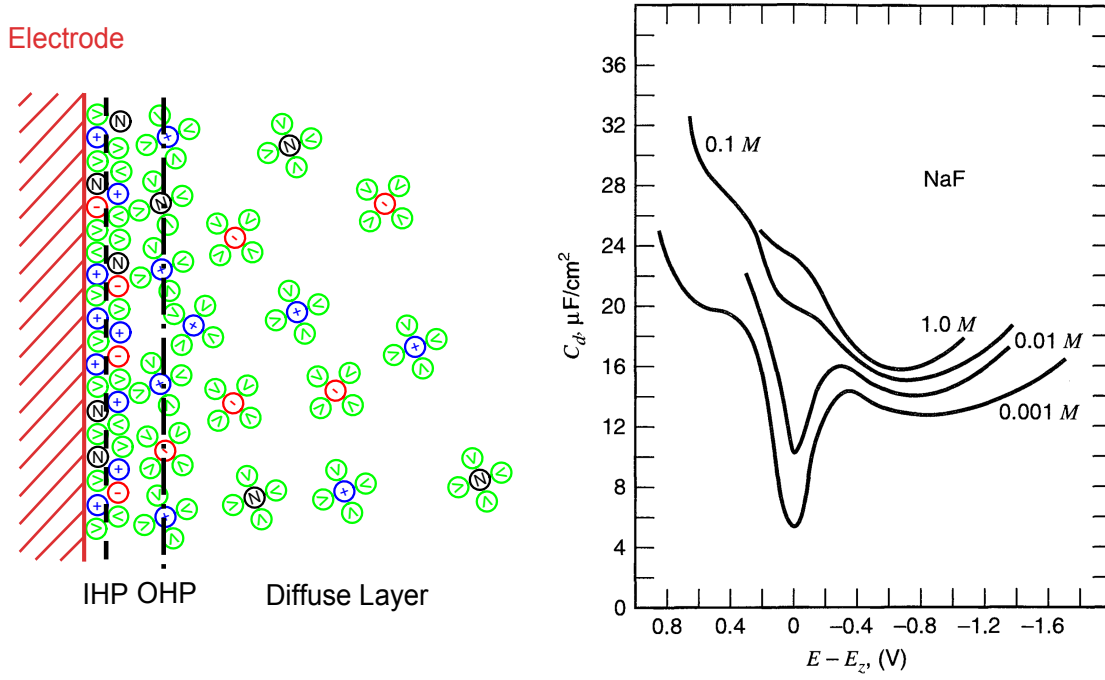


Figure 1.16: (a) Schematic of double layer structure in Grahame's model and (b) Differential capacitance vs. potential for NaF solutions in contact with mercury at 25°C[29].

small roughness Daikhin *et al.* [33] defined roughness function $\tilde{R}(\kappa)$ through

$$C = \tilde{R}(\kappa) C_{GC} \quad (1.39)$$

where C is the real capacitance, and C_{GC} is the diffuse layer capacitance. There is competition between Debye length and surface roughness, thus

$$\begin{aligned} \lim_{\kappa \rightarrow 0} \tilde{R}(\kappa) &= 1 \\ \lim_{\kappa \rightarrow \infty} \tilde{R}(\kappa) &= R \end{aligned} \quad (1.40)$$

where R is the geometrical roughness. When the roughness is small it can be treated as a perturbation, however this theory is only simple for potentials close to E_{pzc} . At larger potentials the uneven surface charge distribution must be taken into account since charge will accumulate at sharp edges or points, and the roughness function will depend on the electrode potential [32].

One approach to model this behaviour in experimental data is to replace the double layer capacitor element in the equivalent circuit with a constant phase element (CPE) (see §1.6.3 for further details).

$$Z = -\frac{1}{(i\omega C)^\alpha} \quad (1.41)$$

The constant phase element can be seen as a measure of the distribution of capacities at the electrode surface. De Levie showed that for $\alpha = 1$ the CPE behaves as a perfect

capacitor at a flat surface, and for $\alpha = 0.5$ a distribution of capacitances on a porous electrode [34, 35]. α can be related to a fractal dimension D_F introduced by Mandelbrot [31] with values between 2 and 3.

$$\alpha = \frac{1}{D_F - 1} \quad (1.42)$$

For a flat surface $\alpha = 1$ and $D_F = 2$; for a porous electrode $\alpha = 0.5$ and $D_F = 3$. While there has been experimental evidence to support these claims [36–43], it may not be the sole origin of depressed semicircles in Nyquist plots [44–46].

Table 1.6: Potentials of zero charge at Pt single crystal and polycrystalline surfaces[47, p. 212]

Electrode	Electrolyte	$E_{pzc} = 0$ V v SHE	$E_{pzc}^{local} = 0$ V v SHE	Adsorption state (Terrace)	Method	Atomic density $\times 10^{15}$ cm^{-2}
Pt(111)	0.1 M HClO ₄	-	0.34	(111)	CV	1.503
	0.1 M HClO ₄	-	0.29	-	"	-
	0.1 M HClO ₄	-	0.27	0	"	-
Pt(110)	0.1 M HClO ₄	-	0.16	(110)-(1x2)	"	0.920
	0.15 M HClO ₄	-	0.18	(110)		
Pt(100)	0.1 M HClO ₄	-	0.25	(100)-1D	"	1.302
PC Pt	0.3 M HF +					
" (pH 2.4)	0.12 M KF	0.185	0.26	-	Titration	-
" (pH 1.0)	NaClO ₄	0.24	-	-	Scrape	-
" (pH 7.0)	NaClO ₄	0.02	-	-	"	-
" (pH 11.0)	NaClO ₄	-0.3	-	-	"	-
"	LiClO ₄ /AN	0.14	-	-	Impedance	-
"	LiClO ₄ /DMSO	0.09	-	-	"	-

1.4.3 Further Developments

The Stern and Grahame models are remarkably successful models considering their simplicity, in particular the use of Poisson-Boltzmann theory (PBT). However, PBT is based on two major assumptions, it is a mean field approach (ion-ion correlations are neglected) [48–52], and the charge carriers are assumed to be infinitely small point charges [53]. Since the 1950's work has been done to include ion-specific behaviour [54–58], the excluded volume effect [59–67], and the dipole nature of the solvent [68–70].

Discussion of these extensions are beyond the scope of this introduction.

1.4.4 Specific Adsorption

Specific adsorption, as mentioned in § 1.4.1.4, is the adsorption of ions on the electrode surface after partially or fully losing their solvation sheath. These ions can have the same or opposite charge to the electrode. It has been observed experimentally that specific adsorption of anions is more common than cations. This makes sense, even with simple electrode models like the free electron gas. The electrode surface is a cation lattice with a sea of free moving electrons, naturally one would expect anions to be preferentially attracted. Specifically adsorbed ions shift the point of zero charge on the electrode surface, which is known as the Esin-Markov effect. Extra charge from the electrode must move to the interface to balance the extra charge due to the specifically adsorbed ions. For cation specific adsorption E_{pzc} moves in the positive direction, negative for anions, which is represented by the Esin-Markov coefficient

$$\beta = \frac{1}{RT} \left(\frac{\partial(\delta E_{pzc})}{\partial \ln a} \right)_{\sigma_M} = \left(\frac{\partial(\delta E_{pzc})}{\partial \mu} \right)_{\sigma_M} \quad (1.43)$$

In aqueous solutions specific adsorption only takes place close to E_{pzc} ; at potentials far from E_{pzc} solvent molecules are too strongly attracted to the surface. Usually, the specific adsorption of ions increases the capacitance of the double layer, whereas the adsorption of organic molecules decreases it [19].

The degree of specific adsorption depends on electrolyte concentration, which can be described as degree of coverage due to monolayer adsorption isotherms. There are three commonly used isotherms [2].

1.4.4.1 Langmuir isotherm

The Langmuir isotherm assumes that there are no interactions between adsorbed species on the surface, that the surface is uniformly smooth, and that at high concentrations the coverage will eventually saturate to form a monolayer of amount Γ_s . Hence the surface excess is

$$\frac{\Gamma_i}{\Gamma_s - \Gamma_i} = \beta_i \alpha_i \quad (1.44)$$

or when written as the fractional coverage of the surface $\theta = \Gamma_i/\Gamma_s$

$$\frac{\theta}{1 - \theta} = \beta_i \alpha_i \quad (1.45)$$

where a_i is the activity of species i in solution and β_i is the energy coefficient, dependent on the standard free energy of adsorption $\Delta \bar{G}_i^0$

$$\beta_i = \exp \left(-\frac{\Delta \bar{G}_i^0}{RT} \right) \quad (1.46)$$

The Langmuir isotherm can also be written in terms of the concentration of species i in solution

1.4.4.2 Temkin isotherm

Including the interactions between the adsorbed ions complicates things further, as the adsorption energy becomes a function of the degree of coverage

$$\Gamma_i = \frac{RT}{2g} \ln(\beta_i a_{i,\infty}) \quad (0.2 < \theta < 0.8) \quad (1.47)$$

where g is parameter related to interaction energy between the adsorbed species.

1.4.4.3 Frumkin isotherm

Frumkin's isotherm is a generalised approach of the previous two isotherms. When g is positive the interaction between the adsorbed ions is attractive, and when g is negative it is repulsive. When $g = 0$ and $\Gamma_i/\Gamma_s = \theta$ equation 1.48a becomes the Langmuir isotherm. Also of note is that the Temkin isotherm is a special case of the Frumkin isotherm, where $\Gamma_i/\Gamma_s = 0.5$. The Frumkin isotherm can be written as

$$\beta_i a_{i,\infty} = \frac{\Gamma_i}{\Gamma_s - \Gamma_i} \exp\left(\frac{2g\Gamma_i}{RT}\right) \quad (1.48a)$$

$$\text{or } \Gamma_i = \frac{RT}{2g} \ln\left(\frac{\Gamma_s - \Gamma_i}{\Gamma_i}\right) \quad (1.48b)$$

1.4.5 Double Layer Corrections

As early as 1933 Frumkin realised that the structure of the double layer and the specific adsorption of ions can affect the kinetics of electrode reactions [71]. For a reaction of the type $O + e^- \rightleftharpoons R$, which is not specifically adsorbed, the ions closest approach is to the electrode is the OHP (Outer Helmholtz Plane). The potential at the OHP, ϕ_2 , is not the same as in the bulk solution, ϕ_s because of the potential drop across the diffuse layer, and this difference manifests itself in two ways. The first is the concentration of the reactant at the OHP is different to the bulk value

$$C_{OHP} = C_\infty \exp\left(-\frac{z_i F \Delta\phi_2}{RT}\right) \quad (1.49)$$

Second, the driving force for the electrochemical reaction is the potential difference between the electrode and the reacting site. At the OHP this value is different, and the apparent rate coefficient for the reduction reaction needs to be corrected thus:

$$k_c = k_{0,t} \exp\left[\frac{-\alpha_c n F (\phi_M - \phi_2)}{RT}\right] \quad (1.50)$$

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and hence the exchange current becomes

$$i_0 = i_0^{exp} \exp \left[\frac{-\alpha_c n F (\phi_M - \phi_2)}{RT} \right] \quad (1.51)$$

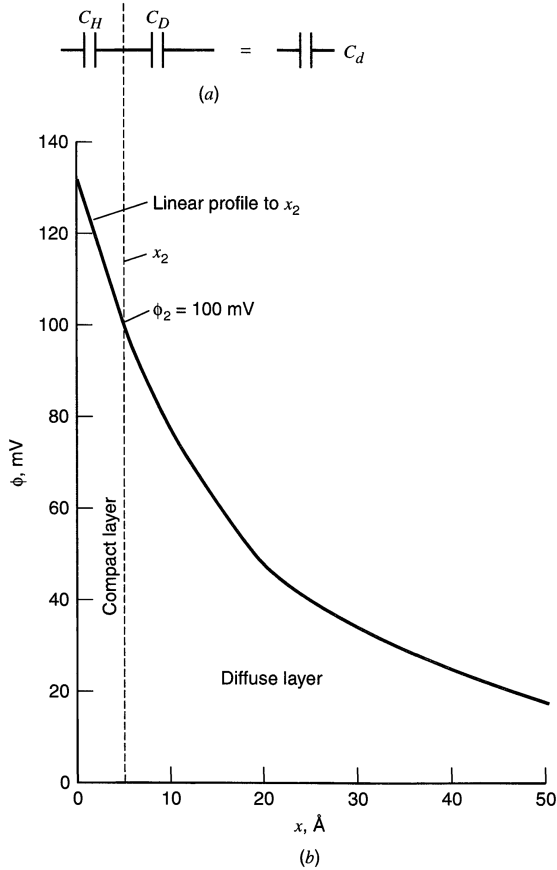


Figure 1.17: A typical potential profile through the solution side of the double layer [1].

When an ion from the supporting electrolyte is *specifically* adsorbed, ϕ_2 is perturbed from the previously calculated value. As mentioned before, specific adsorption of an anion will cause ϕ_2 to be more negative, while specific adsorption of a cation will cause ϕ_2 to be more positive. In theory these effects can be calculated and corrected for, but in practise the distance of the OHP and IHP planes of closest approach and their potentials often cannot be defined, and the majority of calculations are qualitative, rather than quantitative in nature. Specific adsorption of an ion in low concentration can accelerate a kinetic reaction, but at higher levels of adsorption, it may lead to the electrode being partially blocked, inhibiting the reaction. The Frumkin double-layer correction of the observed electrode kinetics is more important at low ionic concentration, high ionic charge and close to the potential of zero charge

(E_{zpc}). This correction can be minimized by using a high concentration of a supporting or inert electrolyte so that most of the potential drops operates in the inner Helmholtz plane, similar to the minimisation of migration in § 1.5.2.

1.5 Mass Transport

The previous section only considered the rate of an electron transfer reaction occurring at the electrode-solution interface. One would expect other processes to occur in this interface and in bulk solution, and contribute to the kinetics of a given reaction. As seen in § 1.3.1 the rate of an electrode reaction can be expressed as

$$\frac{I}{nFA} = k_a [R]_* - k_c [O]_* \quad (1.52)$$

The charge transfer rate is strongly dependent on the electrode potential and the species concentration at the electrode surface. Increasing the potential can increase the rate of charge transfer dramatically since k_a , k_c depend on the potential; but only over a very short distance (0.5 nm) [16]. Some other process or processes are required to bring the reacting species to the electrode surface and remove the products, thus allowing the reaction to continue. These processes are referred to as **mass transport**. Mass transport consists of three different processes **diffusion** – movement of a species due to a concentration gradient; **migration** – the movement of a charged body in an electric field; and **convection** – stirring or hydrodynamic transport through density gradients (*natural convection*) or external forces, e.g. mechanical energy (*forced convection*), and can be described by the Nernst-Planck equation [1].

$$\mathbf{J}_i = -D_i \nabla c_i - \frac{z_i F}{RT} D_i c_i \nabla \phi + c_i \mathbf{v} \quad (1.53)$$

where J_i is the flux of species i ($\text{mol s}^{-1} \text{cm}^{-2}$) at a given position from the surface, D_i is the diffusion coefficient $\text{cm}^2 \text{s}^{-1}$, ∇c_i is the concentration gradient, z_i and c_i are the charge (dimensionless) and concentration (mol cm^{-3}) of species i , $\nabla \phi$ is the potential gradient and $\mathbf{v}$ is the fluid velocity of a volume element in solution. For a simple one dimensional flux this can be represented by:

$$\mathbf{J}_i = -D_i \frac{\partial c_i}{\partial x} - \frac{z_i F}{RT} D_i \mathbf{E} + c_i \mathbf{v}(x) \quad (1.54)$$

where $\mathbf{E} = \delta \phi / \delta x$. Electrochemical analysis is generally more complicated when all three forms of mass transport are present; normally experimental conditions are chosen to render one or two contributions negligible. The addition of a concentrated inert electrolyte (supporting electrolyte) can eliminate measurable migratory effects, and convection can be avoided by preventing stirring and vibrations in the electrochemical cell, mounting the working electrode facing down, antiparallel to gravity, and minimising thermal gradients by controlling the cell temperature. Charge transfer and mass transport are two consecutive processes, hence the slowest step determines the overall rate of reaction. At large applied potentials, the kinetic step occurs rapidly, and the system becomes mass transport limited. Increasing the potential further will increase the rate of electron transfer, but this will have no influence of the overall reaction, resulting in a current that is independent of applied potential (the limiting current i_l). It is possible to write a simple relation for the observed current i as [16]:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_m} \quad (1.55)$$

where i_k is the kinetically controlled current and i_m is the mass transport controlled current. From (1.55) it is clear that the smallest current is dominant.

1.5.1 Diffusion

Diffusion arises from a concentration gradient close to the electrode surface, and thus can effect all species in solution. Fick's first law states that the rate of diffusion is proportional to the concentration gradient [1]:

$$J_i = -D_i \frac{\partial c_i}{\partial x} \quad (1.56)$$

D_i is the proportionality constant, known as the *diffusion coefficient*. In aqueous solutions it commonly has a value between 10^{-6} and $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [2], and generally is determined by mass-transport controlled measurements (see table 1.7). Fick's second law describes the variation of concentration due to diffusion over time

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c}{\partial x^2} \quad (1.57)$$

It can be derived simply from Fick's first law, assuming mass transport balance. For an element of width dx (fig. 1.18), the change in concentration is given by

$$\frac{\partial c_i}{\partial t} = \frac{J_i(x) - J_i(x + dx)}{dx} \quad (1.58)$$

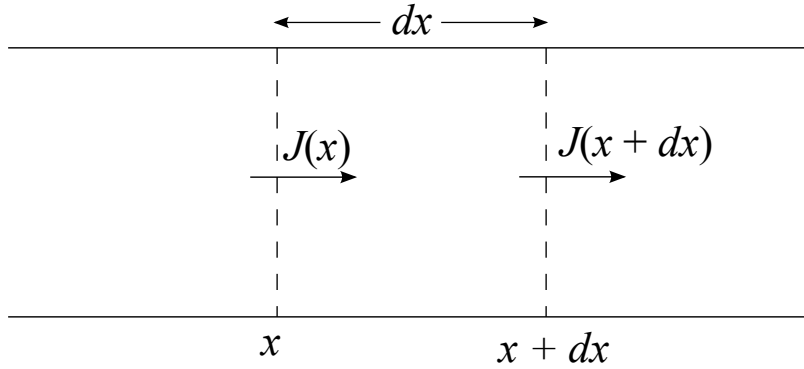


Figure 1.18: Linear diffusion in the x-plane. Diffusion is in the direction opposing the concentration gradient.

We also know that

$$\begin{aligned} J_i(x) - J_i(x + dx) &= J_i(x) + \frac{\partial J_i}{\partial x} dx \\ &= J_i(x) - \frac{\partial}{\partial x} D_i \frac{\partial c}{\partial x} dx \\ &= J_i(x) - D_i \frac{\partial^2 c}{\partial x^2} dx \end{aligned} \quad (1.59)$$

assuming that the diffusion coefficient is constant and does not depend on position;

and by substitution into (1.58) we arrive at Fick's second law

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c}{\partial x^2} \quad (1.60)$$

In two or more dimensions this becomes

$$\frac{\partial c_i}{\partial t} = \nabla \cdot (D_i \nabla c_i) \quad (1.61)$$

or

$$= D_i \nabla^2 c_i \quad (1.62)$$

when D_i is independent of position and/or concentration. At steady state, the concentration is constant, so the left side of equation (1.61) is zero, and we are left with Laplace's equation

$$\nabla^2 c_i = 0 \quad (1.63)$$

The diffusion coefficient appears in many theoretical treatments of electrochemical systems. Only current arising from non-transport related sources (e.g., double-layer charging and redox reactions of adsorbate layers) are independent of the diffusion coefficient [72]; so knowledge of the diffusion coefficients for a given system is almost always a requirement in electrochemistry. Table 1.7 summaries a variety of methods to measure the diffusion coefficient electrochemically. Many of them involve the use of ultra-micro electrodes (UMEs), normally discs, which typically have a radius less than $25\mu\text{m}$.

Table 1.7: Summary of different methods to measure diffusion coefficients [72]

Method	Procedure	Equation	Comments
Methods with $D \propto i$			
Chronoamperometry at disc UME	Measure steady-state current	$D = \frac{i_{ss}}{4nFc_{\infty}r_0}$	$RG \gtrsim 100, 4Dt/r_0^2 > 500$ for 2% planar diffusion contribution to i_{ss}
Chronoamperometry at hemispherical UME	Measure steady-state current	$D = \frac{i_{ss}}{2\pi nFc_{\infty}r_0}$	$RG \gtrsim 100, 4Dt/r_0^2 > 500$ for 2% planar diffusion contribution to i_{ss}
Linear scan voltammetry at disc UME	Measure steady-state current	$D = \frac{i_{ss}}{4nFc_{\infty}r_0}$	$RG \gtrsim 100$, same time criterion as chronoamperometry, but use $\tau \approx E_f - E_{1/2} /v$
Linear scan voltammetry at hemispherical UME	Measure steady-state current	$D = \frac{i_{ss}}{2\pi nFc_{\infty}r_0}$	$RG \gtrsim 100$, same time criterion as chronoamperometry, but use $\tau \approx E_f - E_{1/2} /v$
Methods with $D \propto i^{3/2}$			
Rotating disc electrode	Measure limiting current, i_l as a function of rotation rate ω and plot i_l vs. $\omega^{1/2}$	$D = \left(\frac{\text{slope}}{0.62nFAc_{\infty}v^{-1/6}} \right)^{3/2}$	Use with $10 < \omega < 10,000$
Methods with $D \propto i^2$			
Chronoamperometry at planar electrode	Measure current as a function of time, plot $i(t)$ vs. $t^{-1/2}$	$D = \frac{(\text{slope})^2 \pi}{(nFAc_{\infty})^2}$	Avoid charging current measurements at short times ($t \lesssim 10R_sc_d$), avoid long times (convection, edge effects)

Table 1.7: Summary of different methods to measure diffusion coefficients [72]

Method	Procedure	Equation	Comments
Normalised chronoamperometry at disc UME	Measure current as a function of time and normalise by steady state current. Plot normalised current vs. $t^{-1/2}$	$D = \frac{4r_0^2}{(\text{slope})^2\pi^3}$	Requires only r_0 ; avoid charging current measurements at short times ($t \lesssim 10R_sC_d$)
Chronopotentiometry at planar electrode	Measure transition time at several current densities, find average value of τ	$D = \frac{4i_0^2\tau}{\pi(nFc_\infty)^2}$	Avoid conditions with long transition times (convective effects); less accurate when there are large relative background contributions to the overall current (i.e., low c_∞ , large C_d , short τ)
Linear scan voltammetry at a planar electrode	Measure peak current as a function of scan rate, plot i_p vs. $v^{1/2}$	$D = \frac{(\text{slope})^2}{n^3(2.69 \times 10^5 Ac_\infty)^2}$	Nernstian systems only; avoid scan rates with appreciable nonlinear diffusion; should be considered an approximate method

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1.5.1.1 Cottrellian System

One commonly used technique for studying diffusion limited systems is *chronoamperometry* (see §1.6.1.1). A potential step is applied from a value with no electrode reaction to one where all the electroactive species react. Assuming only an induced diffusion limited current (i.e. no migration or convection) at a uniformly accessible planar electrode the current can be described by semi-infinite linear diffusion:

$$i_d = nFAD \left(\frac{\partial c}{\partial x} \right)_{x=0} \quad (1.64)$$

For simplicity an oxidation (positive) current is considered, with $c = [R]$. To solve Fick's second law we use the following boundary conditions:

$$t = 0, \quad c_0 = c_\infty \quad (\text{no electrode reaction}) \quad (1.65a)$$

$$t \geq 0, \quad \lim_{x \rightarrow \infty} c = c_\infty \quad (\text{bulk solution}) \quad (1.65b)$$

$$\left. \begin{array}{l} t < 0 \\ x = 0 \end{array} \right\} \quad c_0 = 0 \quad (\text{diffusion-limited current } i_d) \quad (1.65c)$$

where c_0 is the concentration at the electrode and c_∞ the bulk concentration. To simplify the problem, the dimensionless concentration is used

$$\gamma = \frac{c_\infty - c}{c_\infty} \quad (1.66)$$

and a Laplace transform (with respect to t) is performed on (1.57), resulting in

$$s\bar{\gamma} = D \frac{\partial^2 \bar{\gamma}}{\partial x^2} \quad (1.67)$$

Equation (1.67) has a general solution of the form [2]

$$\bar{\gamma} = A'(s) \exp \left[-(s/D)^{1/2} x \right] + B'(s) \exp \left[(s/D)^{1/2} x \right] \quad (1.68)$$

The second term does not satisfy the boundary condition (1.65c) ($x \rightarrow \infty, \bar{\gamma} \rightarrow 0$), thus $B'(s) = 0$. In Laplacian space, (1.65c) is

$$x = 0 \quad \bar{\gamma} = -1/s \quad (1.69)$$

and (1.68) becomes

$$A'(s) = -1/s \quad (1.70)$$

Substituting this into the general solution (1.68) remembering that $B'(s) = 0$ gives

$$\bar{\gamma} = -\frac{1}{s} \exp \left[-(s/D)^{1/2} x \right] \quad (1.71)$$

followed by differentiation

$$\left(\frac{\partial \bar{\gamma}}{\partial x}\right) = (sD)^{-1/2} \exp[-(s/D)^{1/2}x] \quad (1.72)$$

Performing an inverse transform on (1.71) results in a description of concentration at a distance x in time (see fig 1.19.a).

$$c = c_{\infty} \left\{ 1 - \operatorname{erfc} \left[\frac{x}{x(Dt)^{1/2}} \right] \right\} \quad (1.73)$$

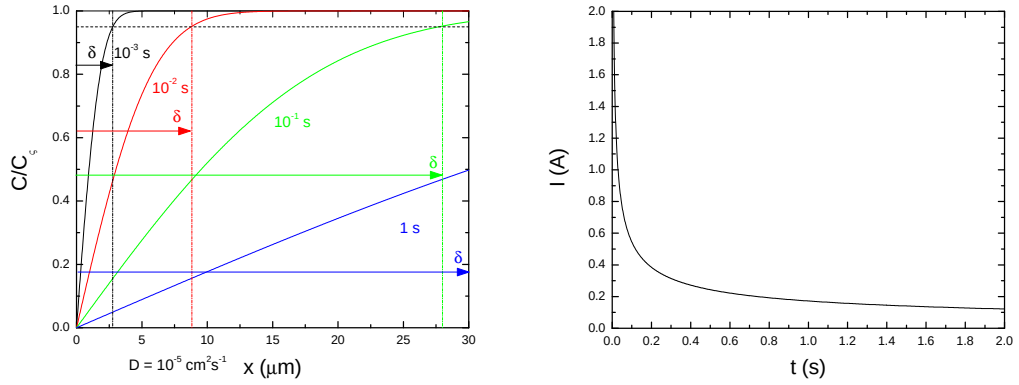


Figure 1.19: (a) Variation of concentration with distance at a planar electrode at different times for $D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (b) Dependence of current with time for $c = 1 \text{ mol l}^{-1}$ and $a = 1 \text{ cm}^2$

Finally, to derive the current at the electrode surface we set $x = 0$ and perform an inverse Laplacian transform on (1.72), to find the concentration gradient

$$\left(\frac{\partial c}{\partial x}\right)_{x=0} = \frac{1}{(\pi Dt)^{1/2}} \quad (1.74)$$

which leads us to the Cottrell equation [73]

$$i(t) = \frac{nFAD^{1/2}c_{\infty}}{(\pi t)^{1/2}} \quad (1.75)$$

Care must be taken using this equation, as at long times the diffusive currents will be disrupted by natural convection, and at short times there is a contribution due to the charging of the double layer. Another issue is that the Cottrell equation describes the zero-time limit [74], the Saito equation [75] addresses the long time limit.

$$i = 4nFc_{\infty}Dr \quad (1.76)$$

where r is the electrode radius. There are more accurate equations that try to bridge this gap [74, 76–88], but most of them are unwieldy and impractical to use. The most

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commonly used of these equations at inlaid disc microelectrodes is the Shoup-Szabo equation [89]

$$|I(t)| = A + Bt^{-1/2} + 0.2732 A \exp\left(\frac{-0.3911 B\pi^{1/2}}{At^{1/2}}\right) \quad (1.77)$$

where $A = \pi FrncD$ and $B = \pi^{1/2}Fr^2ncD^{1/2}$

1.5.2 Migration

In contrast to diffusion, only charged species are affected by migration. In bulk solution, concentration gradients are generally small, and in the absence of convection the total current is carried mainly by migration. Under an applied electric field $\mathbf{E} = \delta\phi/\delta x$ the migration flux behaves as:

$$J_i = -\frac{z_i F}{RT} D \quad (1.78)$$

1.5.3 Conductivity and Mobility

The ability of all ions in a given solution to move in an applied electric field determines the conductivity of the solution. Considering an isolated ion, the force due to the electric field is

$$\mathbf{F} = ze\mathbf{E} \quad (1.79)$$

which is opposed by a frictional/viscous force given by Stokes' equation [2]

$$\mathbf{F} = 6\pi\eta r\mathbf{v} \quad (1.80)$$

where η is the solution viscosity, r the radius of the solvated ion, and $\mathbf{v}$ the velocity. There are other retarding forces such as the asymmetric and electrophoretic effects [2] which are neglected. Therefore the maximum velocity is

$$\begin{aligned} \mathbf{v} &= \frac{ze\mathbf{E}}{6\pi\eta r} \\ &= u\mathbf{E} \end{aligned} \quad (1.81)$$

where u is the ion mobility. To relate the conductivity to mobility we examine the flux of charge between two electrodes of equal area A , first noting that the flux of charge $\mathbf{j}$ is

$$\mathbf{j} = ze\mathbf{v}cN_A \quad (1.82)$$

where ze is the charge of each ion, $\mathbf{v}$ its velocity, and cN_A the number ion density. Substituting $eN_A = F$ for one mole of electrons the flux becomes:

$$\begin{aligned}\mathbf{j} &= z\mathbf{v}cF \\ &= zcuF\mathbf{E}\end{aligned}\tag{1.83}$$

The current i passing through the two parallel plates mentioned above, with a potential difference $\Delta\phi$ is

$$\mathbf{i} = \mathbf{j}A = \kappa \frac{\Delta\phi A}{l} = \kappa \mathbf{E}A\tag{1.84}$$

where κ is the conductivity, and l the distance between electrodes. Combining (1.83) and (1.84) indicates that for each ion

$$\kappa_i = z_i c_i u_i F\tag{1.85}$$

Therefore the solution, or measured conductivity is

$$\kappa = F \sum_i |z_i| c_i u_i\tag{1.86}$$

The molar conductivity of an ion λ_i is

$$\lambda_i = \frac{\kappa_i}{c_i} = z_i u_i F\tag{1.87}$$

and the electrolyte molar conductivity Λ is

$$\Lambda = F \sum_i \lambda_i = \sum_i \frac{\kappa_i}{c_i}\tag{1.88}$$

Examining equations (1.87) and (1.88) we can see that conductivity measurements cannot distinguish ions in solution. For complicated solutions, conductivities or mobilities of one or more ions need to be known *a priori* to determine all ionic conductivities. To complicate things further, ionic conductivities can vary with solution composition and concentration.

Now we ask the question, what is the relationship between mobility and the diffusion coefficient? Since a concentration gradient is also a chemical potential gradient, and for a sufficiently dilute ion, i [2], we can describe it as

$$\mu_i = \mu_i^\ominus + RT \ln c_i\tag{1.89}$$

where $\mu_i^\ominus$ is the standard chemical potential. Differentiating with respect to the distance x

$$\left(\frac{\partial \mu_i}{\partial x}\right)_{P,T} = \frac{RT}{c_i} \left(\frac{\partial c_i}{\partial x}\right)_{P,T}\tag{1.90}$$

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Thus the force experienced by an ion i is

$$\begin{aligned}\mathbf{F} &= - \left(\frac{\partial \mu_i}{\partial x} \right) \\ &= - \frac{RT}{c_i} \left(\frac{\partial c_i}{\partial x} \right)_{P,T}\end{aligned}\tag{1.91}$$

From (1.83), the number flux of ions is

$$\mathbf{J}_i = \frac{j_i}{z_i e} = c_i u_i \mathbf{E}\tag{1.92}$$

Substituting (1.80) into (1.92) we arrive at

$$\mathbf{J}_i = \frac{c_i u_i \mathbf{F}}{z_i e}\tag{1.93}$$

Combining (1.91) and (1.92) gives

$$\mathbf{J}_i = - \frac{u_i RT}{z_i F} \left(\frac{\partial c_i}{\partial x} \right)_{P,T}\tag{1.94}$$

and comparing with Fick's first law leads to the Einstein relation:

$$D_i = \frac{u_i RT}{z_i F}\tag{1.95}$$

The Einstein relation shows that the diffusion coefficient is directly proportional to the mobility, and from equations (1.87) and (1.95) we can derive the Nernst-Einstein relation

$$\lambda_i = \frac{z_i^2 F^2 D_i}{RT}\tag{1.96}$$

Finally, from (1.81) and (1.95) we can obtain the Stokes-Einstein relation

$$D_i = \frac{k_B T}{6\pi\eta r}\tag{1.97}$$

Using these relations it is possible to calculate diffusion coefficients from measurements of mobility, conductivity or viscosity.

1.5.4 Convection

Convection is the motion of a fluid under the action of a force. There are two kinds of convection, *natural convection* arises from thermal and density gradients, and are common to all solutions. The second is *forced convection*) which is due to an external forces, such as provided by mechanical stirring or magnetohydrodynamic stirring. The

velocity field in a fluid can be described by the Navier-Stokes equation

$$\rho \left(\underbrace{\frac{\partial \mathbf{v}}{\partial t}}_{\text{Unsteady acceleration}} + \underbrace{\mathbf{v} \cdot \nabla \mathbf{v}}_{\text{Convective acceleration}} \right) = \underbrace{-\nabla p}_{\text{Pressure gradient}} + \underbrace{\mu \nabla^2 \mathbf{v}}_{\text{Viscosity}} + \underbrace{\mathbf{f}}_{\text{Other body forces}} \quad (1.98)$$

Two kinds of fluids are flows most relevant to electrochemistry, *laminar flow*, and *turbulent flow*. In a laminar flow the fluid velocity is smooth and steady, and occurs in separate layers or laminae, hence it is referred to as laminar flow. Typically in pipes the flow is laminar, with a zero fluid velocity at the walls and a parabolic maximum at the center of the pipe [1]. A flow is called turbulent when the fluid motion is chaotic and unsteady, with only an average net velocity in one direction. Before any description of the hydrodynamic system it is convenient to introduce some dimensionless numbers useful in studying mass transport.

1.5.4.1 Reynolds Number

$$\text{Re} = \frac{vl}{\nu} \quad (1.99)$$

where v is the flow velocity, l is the characteristic length scale and ν is the kinematic viscosity. The Reynolds number gives a measure of the ratio of inertial forces $\rho v^2/l$ to viscous forces $\mu v/l^2$. When the Reynolds number is small, viscous forces outweigh inertial forces, and under such conditions the flow is laminar, whereas the flow becomes turbulent at large Reynolds numbers. For a pipe, the flow is laminar for $\text{Re} < 2300$ and becomes turbulent for $\text{Re} > 4000$ [90].

1.5.4.2 Schmidt number

$$\text{Sc} = \frac{\nu}{D} \quad (1.100)$$

where D is the diffusion coefficient. The Schmidt number is the ratio of momentum diffusivity (viscosity) and mass diffusivity, and is used to characterize fluid flows in which there are simultaneous momentum and mass diffusion convection processes. It relates the relative thickness of the hydrodynamic layer and mass-transfer boundary layer. For aqueous solutions it is typically $\text{Sc} \approx 10^3$ [2].

1.5.4.3 Peclet number

$$\text{Pe} = \frac{lv}{D} = \text{Re} \cdot \text{Sc} \quad (1.101)$$

The Peclet number represents the relative contributions of transport by convection and by diffusion. It is the the ratio of the rate of advection by the flow to the rate of diffusion. It is the product of the Reynolds number and the Schmidt number.

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1.5.4.4 Sherwood number

$$\text{Sh} = \frac{Jl}{D(c_\infty - c_0)} = \frac{1}{\delta} = \frac{k_d l}{D} \quad (1.102)$$

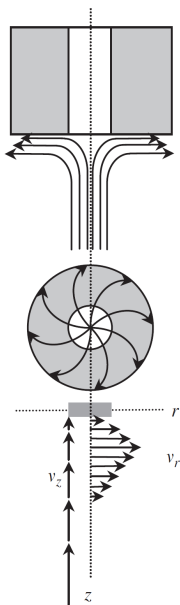
where k_d is the mass transfer coefficient in units m s^{-1} . The Sherwood number is the ratio of convective to diffusive mass transport.

1.5.4.5 Hydrodynamic layer thickness

$$\delta_H = \left(\frac{\nu}{D}\right)^{1/3} \delta \quad (1.103)$$

where δ is the diffusion layer thickness. The hydrodynamic layer thickness is another useful parameter for defining the hydrodynamic system, all the velocity gradient is assumed to occur in this layer. It is important to note that the hydrodynamic layer and the diffusion layer are quite different. For a typical aqueous solution, $D \approx 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $\nu \approx 10^{-2} \text{ cm}^2 \text{ s}^{-1}$, and $\delta_H = 10\delta$, and therefore it can be assumed there is little or no convection in the diffusion layer.

1.5.5 The rotating disc electrode



The rotating disc electrode experiment is the most widely used hydrodynamic electrode to control the diffusion layer thickness in electrochemistry [91]. It consists of a disc electrode embedded into an insulating support (normally PTFE), and is then rotated around its vertical axis. The fluid is flung radially from the electrode surface and fresh solution is dragged vertically upwards towards the electrode (see fig. 1.20). The electrode is uniformly accessible and in the treatment by von Karman and Cochran [92, 93], has no edge effects. Levich solved the steady state system producing what is now called the Levich equation [12] relating the limiting current to the rotation speed:

$$i_{lim} = 0.621nFAD^{2/3}\nu^{-1/6}C_\infty\omega^{1/2} \quad \omega \text{ in rad s}^{-1} \quad (1.104a)$$

$$i_{lim} = 1.554nFAD^{2/3}\nu^{-1/6}C_\infty\omega^{1/2} \quad \omega \text{ in Hz} \quad (1.104b)$$

Figure 1.20: Streamlines and flow velocities at an RDE [91].

where n is the number of electrons transferred, F is Faraday's constant, D is the diffusion coefficient, ν is the kinematic viscosity, related to the dynamic viscosity η_v by $\nu = \eta_v/\rho$, c_∞ is the bulk ion concentration, and ω is the rotation speed of the RDE. Limiting

currents generated via linear sweep/steady-state voltammograms (see § 1.6.2 at an RDE) are used to gather information about the kinetics of a redox reaction. If the redox reaction is reversible, then the limiting current is proportional to $\omega^{1/2}$, however

if the shape and the voltammogram (I-V curve) is dependent on ω then the redox reaction is kinetically limited. When the limiting current is measured at series of fixed potentials for a range of rotation speeds, the kinetic constant can be extracted the Koutecký-Levich equation [91].

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{0.201FAD^{2/3}\nu^{-1/6}c_\infty\omega^{1/2}} \quad (1.105)$$

A plot of i^{-1} against $\omega^{-1/2}$ should be linear for a mass transport controlled system, and the intercept should yield i_k^{-1} . From a series of Koutecký-Levich plots at various potentials, the dependence of the kinetic rate constant can be measured.

1.6 Measurement Techniques

1.6.1 Pulse Methods

1.6.1.1 Chronoamperometry

Chronoamperometry involves the application of a potential step, and measuring the current transient at that potential over time. The Cottrell equation was derived in § 1.5.1.1 and relates the current transient measured to $t^{-1/2}$

$$i = \frac{nFAD^{1/2}c_\infty}{(\pi t)^{1/2}} \quad (1.106)$$

The initial potential at the electrode is held at value where there is no electrolysis of the active species (see fig. 1.21) followed by a step to the potential of interest.

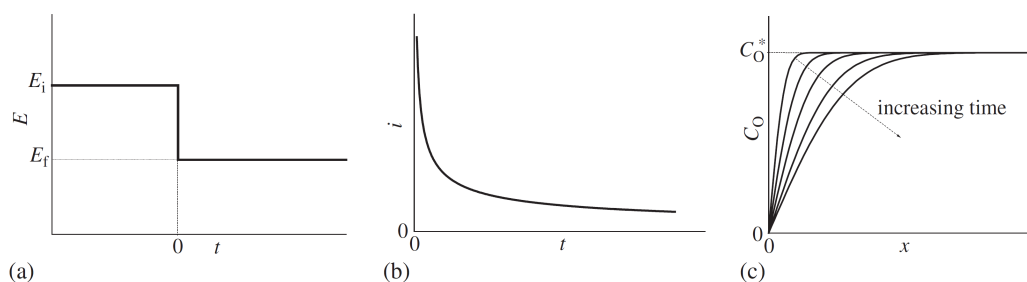


Figure 1.21: Chronoamperometry: (a) application of a potential step, (b) the current response, and (c) the concentration profile close to the electrode [91].

Chronoamperometry can be used to probe reversible and irreversible systems, table 1.8, however there are a number of issues that limit its use at very short times, and at long times:

Double layer charging At short times, there is a contribution from the double layer charging current, e.g. for a simple RC circuit the current response to a potential step is $i_c = \Delta E/R \exp(-t/RC)$. Clearly this can be a large component at short times, but decays faster than the $t^{-1/2}$ Cottrell current.

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Table 1.8: Current response of a Cottrellian system after a potential step inducing an $R - ne^- \rightarrow O$ with only R initially present in solution.

	Current I (A)
Reversible	$\frac{nFAD[O]_{\infty}}{(1 + \theta)(\pi Dt)^{1/2}}$
Irreversible	$nFAD[O]_{\infty} \exp[k_c^2/D] \operatorname{erfc}\left(\frac{k_c t^{1/2}}{D^{1/2}}\right)$
Irreversible small t	$nFAD[O]_{\infty} \left(1 - \frac{2k_c t^{1/2}}{(\pi D)^{1/2}}\right)$
	$\theta = [O]_{\infty}/[R]_{\infty}$

Potentiostat response The Cottrell equation predicts very large currents at short times, the measured current response is limited by the compliance of the measuring electronics and may not be a true representation of the current. The measured transient is also limited by the time response of the potentiostat, along with the sampling rate.

Natural convection At long times natural convection disturbs the diffusion layer, invalidating the assumptions of the Cottrell equation. There have been a number of experiments in microgravity and very stable temperatures to avoid this problem and measure long-time currents [94].

As mentioned previously, the Shoup-Szabo equation [89] is a more accurate description of the current pulse at inlaid disc microelectrodes, and is useful for high accuracy diffusion coefficient measurements [95].

$$|I(t)| = A + Bt^{-1/2} + 0.2732 A \exp\left(\frac{-0.3911 B \pi^{1/2}}{At^{1/2}}\right) \quad (1.107)$$

where $A = \pi F a n c D$ and $B = \pi^{1/2} F a^2 n c D^{1/2}$

1.6.1.2 Chronocoulometry

Another approach to measure the response of a system to a voltage pulse is to record the charge accumulation at the electrode with time, referred to as chronocoulometry. For a cottrellian system, the charge response is the time integral of the Cottrell equation

$$Q_F(t) = \frac{2nFAD^{1/2}c_{\infty}}{\pi^{1/2}} t^{1/2} \quad (1.108)$$

The measured charge, Q_m is the sum of three components, the charge due to the redox reaction (faradaic response), the double layer charging, and the the faradaic response due to an adsorbed surface excess Γ_0 of the electroactive species $Q_m = Q + Q_{dl} + nF A \Gamma_0$

If a reverse voltage pulse is applied immediately after the first pulse, (at time $t = \tau$) then the charge response with time is

$$Q_R(\theta) = \frac{2nFAD^{1/2}c_\infty}{\pi^{1/2}}\theta^{1/2} \quad , \quad t < \tau \quad (1.109)$$

where $\theta = \tau^{1/2} - t^{1/2} + (t + \tau)^{1/2}$

The discharge due to the relaxation of the system includes the double layer discharge, but now there is no adsorption coefficient. Using this technique it is possible to measure the adsorption by plotting $Q_F(t^{1/2})$ and $Q_R(\theta)$ and subtracting the intercepts (fig. 1.22).

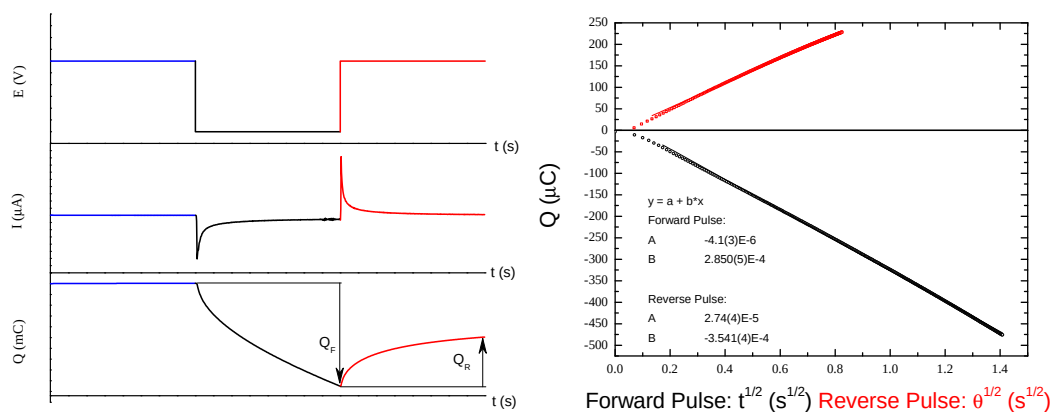


Figure 1.22: Double pulse chronocoulometry: (a) Voltage pulse and current and charge responses, Q_F and Q_R are the forward and reverse pulse charges, (b) a plot of $Q_F(t^{1/2})$ and $Q_R(\theta)$ for the reduction of 0.1 M nitrobenzene in 0.5 M TBAP/ACN. The non-linearity at short times is due to the response of the potentiostat.

$$\Delta Q = Q_{F,t=0} - Q_{R,t=0} = nFA\Gamma_0 \quad (1.110)$$

1.6.2 Sweep Methods

Sweep methods, in particular voltammetry are the most commonly used techniques in electrochemistry to measure the kinetic and mass transport characteristics of a system [2]. Sweep voltammetry involves applying a continuous voltage sweep while measuring the voltage response, continually altering the concentration gradient at the electrode (see fig. 1.26). The two main kinds are *linear sweep* and *cyclic voltammetry*. In linear sweep voltammetry (LSV), the voltage is swept from an initial potential E_{init} to a final potential E_{final} , whereas in cyclic voltammetry (CV), the voltage is swept from an initial potential E_{init} to a potential E_λ and then reversed to E_{final} (see figs. 1.23, 1.24, and 1.25). The sweep rate v can be from 10 mV s^{-1} to 1000 V s^{-1} for millimetre sized electrode [1]. Cyclic voltammetry is useful in identifying the number of species in solution, along with studying the kinetics, mass transport, and any chemical steps.

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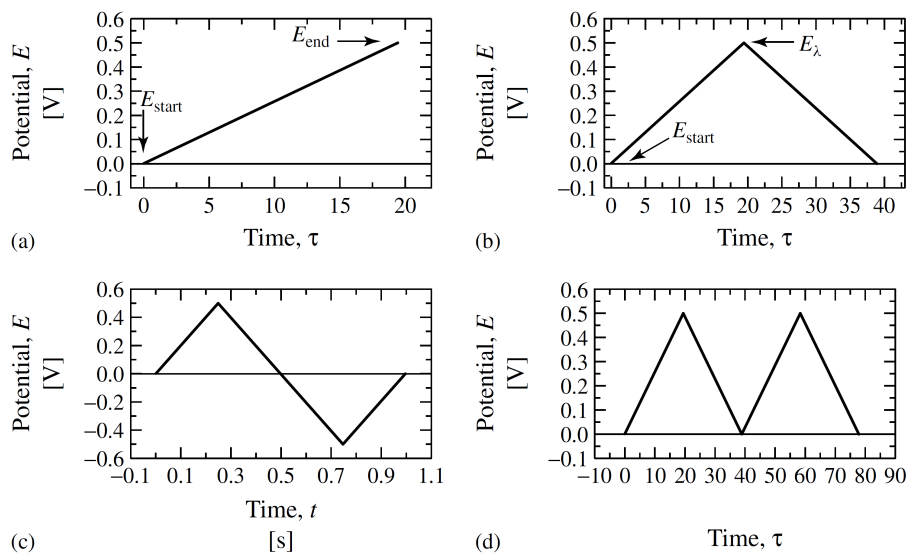


Figure 1.23: (a) Voltage sweeps for linear sweep voltammetry and (b-d) cyclic voltammetry [91].

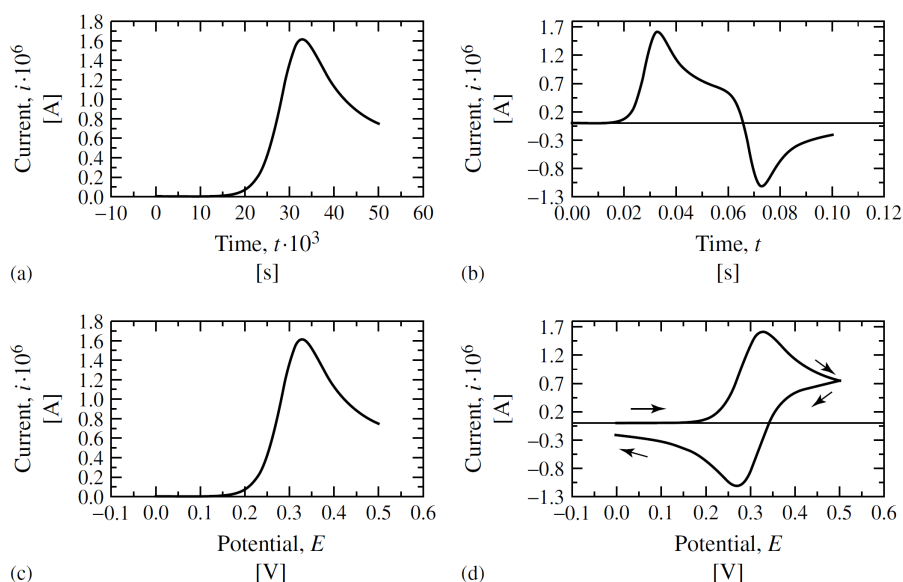


Figure 1.24: Typical results of LSV (left) and CV (right) experiments plotted versus time (a, b) or potential (c, d) [91].

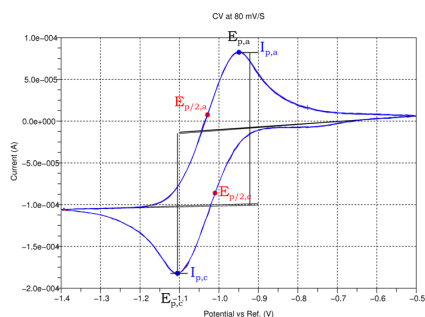


Figure 1.25: A typical IV from a CV sweep using 0.1 M nitrobenzene in 0.5 M TBAP/ACN.

1.6.2.1 Cyclic Voltammetry

In figure 1.26 following points 1-7, species O is consumed at the electrode and a reduction current is observed. The current increases from steps 1-3 while it is kinetically controlled or under mixed control. Once the potential reaches point 3 the rate of reduction by the kinetic current matches the rate of replacement by mass transport, for larger potentials the reactant is depleted faster than can be replenished by mass transport creating a depletion region (the diffusion layer) and the current decreases forming a peak. From points 8-10, O is regenerated by oxidation of R and an oxidation current is observed, and the same diffusion limited peak appears at point 8. The change of sign in the current is directly related to the inversion of the concentration gradient for O at the electrode surface: the gradient is positive for points 1-7 and negative for points 8-10.

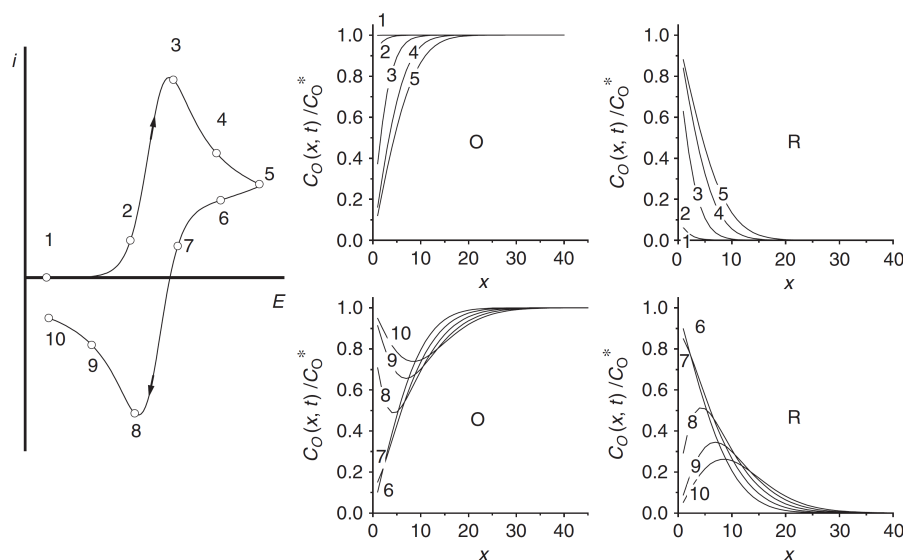


Figure 1.26: Cyclic voltammogram and corresponding O and R concentration profiles for diffusion to a planar electrode [91].

For a reversible reaction of the type $O + e^- \rightleftharpoons R$ the reduction peak current is defined by [2]

$$i_{p,c} = -2.69 \times 10^5 n^{3/2} A D_O^{1/2} [O]_{\infty} v^{1/2} \quad (1.111)$$

where n is the number of electrons transferred, A is the electrode area, D_O is the diffusion coefficient of O, $[O]_{\infty}$ is the bulk concentration of O, and v is the voltage sweep rate. To determine the peak currents it is important to subtract the background current as in fig. 1.25. When the background current baseline is unclear it is possible to use this relation instead to compensate for the faradaic response of the species [96]

$$\left| \frac{I_{p,a}}{I_{p,c}} \right| = \frac{(I_{p,a})_0}{I_{p,c}} + \frac{0.485(I_{\lambda})_0}{I_{p,c}} + 0.086 \quad (1.112)$$

For a reaction to be reversible there are a number of conditions that must be met

1. ELECTROCHEMICAL PHENOMENA

including that the ratio of the cathodic and anodic peaks are the same (i.e. that $[O]_*$ and $[R]_*$ at the electrode are the same, which is not the case if there is a follow up homogeneous reaction), that the charge transfer coefficient is larger than the mass transfer coefficient, that there is a well defined spacing between the oxidation and reduction peak voltages, and that the peak positions are independent of sweep rate v .

$$\left| \frac{I_{p,c}}{I_{p,a}} \right| = 1 \quad (1.113)$$

and

$$k_s = \frac{i_0}{nFAC_\infty} \quad (1.114)$$

where $k_d = \sqrt{\frac{Dv}{\pi}}$

$$|E_p - E_{p/2}| = \frac{56.5\text{mV}}{n} \quad (1.115)$$

With this in mind, for a quasi-reversible system, it is possible to drive it to irreversibility by increasing the sweep rate v . Irreversible systems can be treated similarly to reversible ones, the peak potential is now

$$i_{p,c} = -2.99 \times 10^5 n (\alpha_c n')^{1/2} A D_0^{1/2} [O]_\infty v^{1/2} \quad (1.116)$$

where α_c is the cathodic charge transfer coefficient and n' is the number of electrons transferred in the rate determining step. The peak current is still proportional to $v^{1/2}$, but now the peak voltage is dependent on sweep rate

$$\frac{dE_p}{d \log v} = \frac{29.6\text{mV}}{\alpha n'} \quad (1.117)$$

1.6.3 AC Impedance Methods

Linear sweep or potential step techniques described above normally drive the system electrodes far from equilibrium. In contrast, impedance methods are based on perturbation of the electrochemical cell with an alternating signal of small magnitude allowing measurements at equilibrium or steady state. There are a variety of perturbations that can be used including applied potential, applied current, rotation rate at an RDE [91], and applied magnetic fields [97]. As long as the perturbations are sufficiently small the response can be regarded as linear.

A typical perturbation used is a small sinusoidal voltage signal.

$$V(t) = V_0 \sin \omega t \quad (1.118)$$

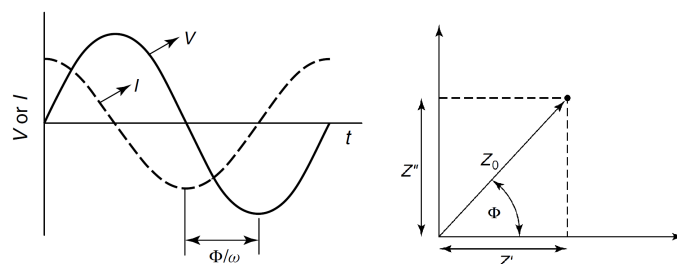


Figure 1.27: (a) A sinusoidal voltage perturbation and the current response and (b) the impedance representation in the complex plane [91].

where $\omega = 2\pi f$ The current response will be

$$I(t) = I_0 \sin(\omega t + \Phi) \quad (1.119)$$

where Φ is the phase shift. Analogous to Ohm's law, the complex impedance is

$$Z = \frac{V(t)}{I(t)} \quad (1.120)$$

which can be written as

$$Z = Z_0 (\cos \Phi + i \sin \Phi) = Z' + iZ'' \quad (1.121)$$

where $Z_0 = V_0/I_0$ is the magnitude and Φ is the phase shift, or using Euler's relationship

$$Z = Z_0 e^{i\Phi} \quad (1.122)$$

1.6.3.1 AC Voltammetry

AC voltammetry is an extension of cyclic voltammetry, where a dc ramp with a comparatively slow sweep rate and an ac signal are superimposed and applied to a working electrode, and the response ac current and its phase angle are registered. In this way a curve is measured that is the first derivative of the cyclic voltammogram (fig. 1.28).

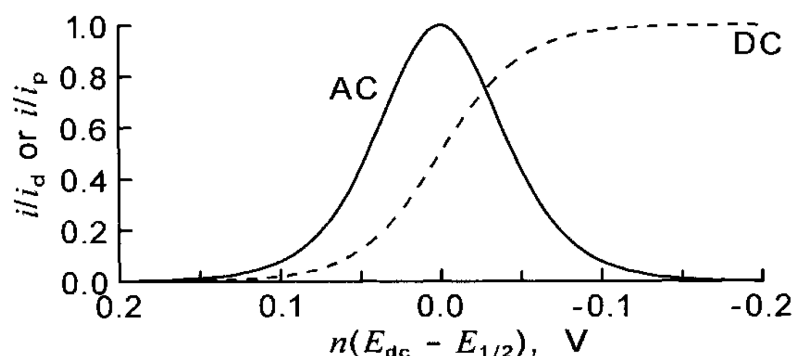


Figure 1.28: I-V curves for AC and DC voltammetry [19].

1. ELECTROCHEMICAL PHENOMENA

The amplitude of the ac current can be described by

$$i = \frac{\Delta E}{Z_f} = \frac{n^2 F^2 A \omega^{1/2} D^{1/2} c_* \Delta E}{4RT \cosh^2(a/2)} \quad (1.123)$$

where $a = nF/RT(E_{dc} - E_{1/2})$ and ΔE is the ac voltage amplitude, and the peak current is given by

$$i_p = \frac{n^2 F^2 A \omega^{1/2} D^{1/2} c_* \Delta E}{4RT} \quad (1.124)$$

It is the cosh term in (1.123) that gives an ac voltammogram its characteristic bell shape. Distinguishing between the in phase and out of phase components can separate the resistive (in phase) components from the capacitive (out of phase) components.

1.6.3.2 Equivalent circuits

Any electrochemical cell can be modelled with an equivalent electrical circuit that consists of resistors, capacitors and sometimes inductors (table 1.9). The most commonly used one in electrochemistry is the Randles circuit which considers the response of the charge transfer resistance R_{ct} in series with the Warburg diffusion resistance Z_W , both in parallel with the double layer capacitance C_{DL} and all three in series with the solution resistance R_s . The high frequency response is predominantly from the charge transfer resistance and double layer capacitance, as seen by the semicircle in the Nyquist plot (fig. 1.30.a). Diffusion dominates at low frequencies, which appears as the straight line, and is described by the Warburg resistance (table 1.9). By using simple circuits like this, it is possible to measure the kinetics and mass transport of a system, and the double layer capacitance. The current response of the system to the voltage perturbation is measured for a range of frequencies, and Nyquist plots or Bode plots are used to fit the response with an appropriate equivalent circuit.

1.6.3.3 Constant phase element

A circuit element called the constant phase element (CPE) was introduced [98] to model depressed arcs in Nyquist plots (fig. 1.30.b). As shown in table 1.9 the impedance of a CPE is

$$Z = -\frac{1}{(i\omega C)^\alpha} \quad (1.125)$$

where α is the dispersion factor, and similar to a capacitor its phase is frequency independent. Generally α is a value between 0.5 and 1 [2], and when $\alpha = 1$ a CPE behaves as a capacitor. At other values the phase shift is no longer $\pi/2$ and a depressed semicircle is seen for Nyquist plots of a resistor and CPE in parallel. The origin of the depressed arcs is still controversial and was discussed briefly in § 1.4.2 in relation to surface roughness.

Table 1.9: Common circuit elements and their impedances

Element	Impedance
R	R
L	$i\omega L$
C	$-\frac{1}{i\omega C}$
CPE	$-\frac{1}{(i\omega C)^\alpha}$
RC in series	$R - \frac{i}{\omega C}$
RC in parallel	$\frac{1}{Z} = \frac{1}{R} - i\omega C$
Finite Warburg short circuit	$R_0 \frac{\tanh([i\omega\delta^2/D]^P)}{[i\omega\delta^2/D]^P}$
Finite Warburg open circuit	$R_0 \frac{\cotanh([i\omega\delta^2/D]^P)}{[i\omega\delta^2/D]^P}$ Where $\delta^2/D = W_{sT}$

1.6.3.4 Kramers-Kronig Relations

To ensure the amplitude of the perturbation used is not too large, the linearity of the systems response can be checked with the Kramers-Kronig relations [91]. The imaginary component can be calculated from real component using

$$Z''(\omega) = -\frac{2\omega}{\pi} \int_0^\infty \frac{Z'(x) - Z'(\omega)}{x^2 - \omega^2} dx \quad (1.126)$$

and the real component from the imaginary from

$$Z'(\omega) = Z'(\infty) + \frac{2}{\pi} \int_0^\infty \frac{xZ''(x) - \omega Z''(\omega)}{x^2 - \omega^2} dx \quad (1.127)$$

Any differences between the measured component and the Kramers-Kronig transformed component are due to non-linearities in the system.

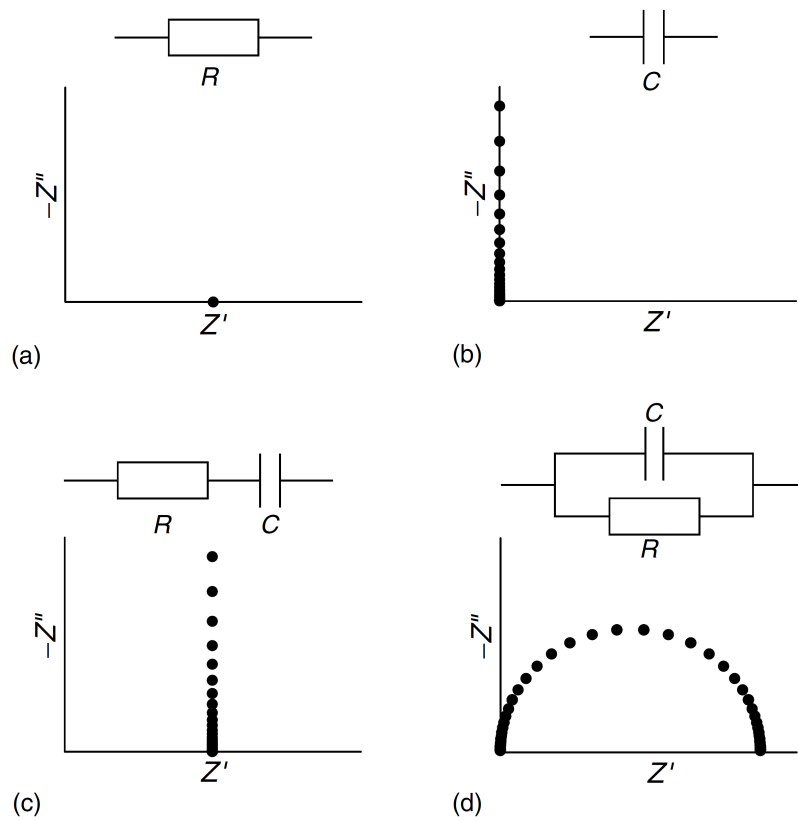


Figure 1.29: Nyquist plots for some circuit elements [98].

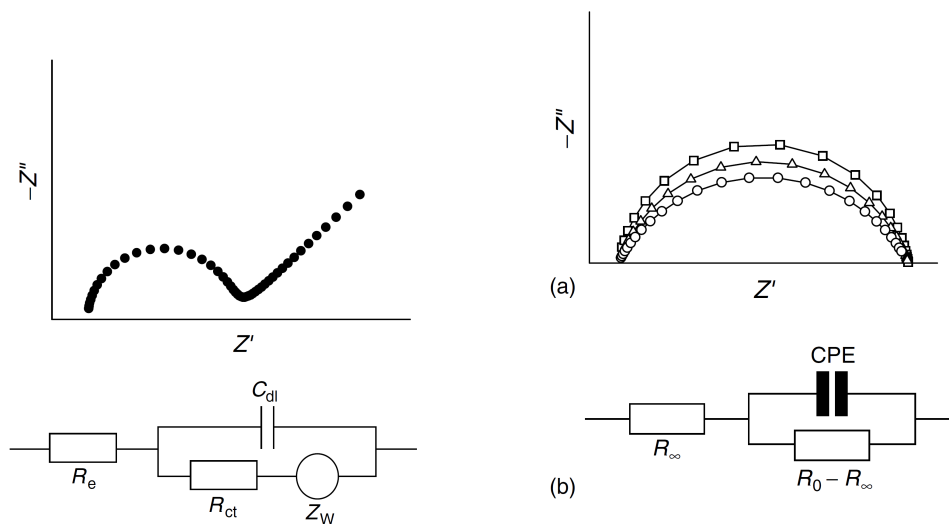


Figure 1.30: (a) Randles circuit and Nyquist plot for reversible electrochemical system with diffusion-limited behavior at low frequencies. (b) Frequency dispersion due to a CPE for $\alpha = 0.9, 0.8, \text{ and } 0.7$.

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Chapter 2

Magneto-electrochemistry

2.1 Magnetic fields

Magnetic fields are created in some reference frame by charges moving relative to the frame. A flux of charge or current density, $\mathbf{J}(\mathbf{x})$, generates a magnetic flux density $\mathbf{B}(\mathbf{x})$ described by the Biot-Savart law [1]

$$\mathbf{B}(\mathbf{x}) = \frac{\mu}{4\pi} \int \frac{\mathbf{J}(\mathbf{x}') \times \mathbf{x} - \mathbf{x}'}{|\mathbf{x} - \mathbf{x}'|^3} d\mathbf{x}' \quad (2.1)$$

The magnetic moment $\mathbf{m}$ is a measure of the degree of alignment of a magnet to a magnetic field $\mathbf{B}$ via a torque τ , and is one of the methods used to define $\mathbf{B}$ [1]. The torque is

$$\tau = \mathbf{m} \times \mathbf{B} \quad (2.2)$$

and its energy is

$$U = -\mathbf{m} \cdot \mathbf{B} \quad (2.3)$$

Normally, the magnetic moment refers to the magnetic dipole moment of the system, which is the second order expansion of the multipolar field. By Gauss's Law

$$\nabla \cdot \mathbf{B} = 0 \quad (2.4)$$

the first term is zero, i.e. there are no magnetic monopoles, and higher orders can be neglected over long range, where the second term is dominant; its field drops off as r^{-3} compared to the more rapid r^{-4} decay for the quadrupole moment. The origin of magnetic moments are twofold, the first is the motion of electric charges, as described by Ampere's law

$$\nabla \times \mathbf{B} = \mu \mathbf{J} \quad (2.5)$$

where μ is material permeability, $\mathbf{J}$ is the related current density; Biot-Savart's law is consistent with both Gauss' law and Ampere's law. One example using Ampere's law

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is the magnetic moment produced by an electric charge moving along a circular path

$$\mathbf{m}_{circ} = -\frac{1}{2}q\mathbf{r} \times \mathbf{v} \quad (2.6)$$

where q is the electric charge, $\mathbf{r}$ is the radius of the circular path, and $\mathbf{v}$ is the instantaneous velocity of the charge.

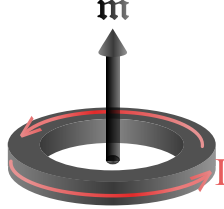


Figure 2.1: The equivalence of a circulating current $\mathbf{I}$ and a magnetic moment $\mathbf{m}$

For an arbitrary current distribution, the moment is

$$\mathbf{m} = \frac{1}{2} \int \mathbf{r} \times \mathbf{J} dV \quad (2.7)$$

The second source is the intrinsic magnetism of elementary particles such as the electron. The magnetic moment of an electron is

$$\mathbf{m}_s = -g_S \mu_B s / \hbar \quad (2.8)$$

where g_S is the spin g-factor ≈ 2 , μ_B is the Bohr magneton, and s is the spin angular momentum of the electron. For an atom the spin angular momentum $\mathbf{S}$ is the sum of all individual spin momenta; likewise the atomic orbital angular momentum $\mathbf{L}$ is the sum of individual orbital momenta, and the total angular momentum is $\mathbf{J} = \mathbf{L} + \mathbf{S}$. Then the magnitude of the dipole moment of a free atom in space is

$$\mathbf{m}_{atom} = g_J \mu_B \sqrt{J(J+1)} \quad (2.9)$$

where g_J is the Landé g-factor

$$g_J \approx 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \quad (2.10)$$

and for a spin-only moment, the magnetic moment becomes

$$\mathbf{m}_{spin-only} = g_S \mu_B \sqrt{J(J+1)} \quad (2.11)$$

It is important to know what the moment is, and its sources since it is fundamental to the generation of magnetic fields, and how this relates to the other vector fields in magnetism. The magnetisation is one such vector field, and is defined as the number

of magnetic moments per unit volume in a sample. It can be written as

$$\mathbf{M} = \frac{N}{V} \mathbf{m} = n \mathbf{m} \quad (2.12)$$

where N is the number of magnetic moments in the sample, V is the sample volume, and n is the number density of moments. The effect of magnetisation is to induce bound current densities inside a material

$$\mathbf{J}_b = \nabla \times \mathbf{M} \quad (2.13)$$

and a bound surface current

$$\mathbf{K}_b = \mathbf{M} \times \hat{\mathbf{n}} \quad (2.14)$$

They are referred to as bound current densities because when a material is magnetised, the electrons remain bound to their respective atoms, but behave as if they were orbiting the nucleus in a particular direction, which creates a microscopic current. Summing up all the atomic currents results in an effect like a macroscopic current, circulating around the magnetised object. The magnetisation $\mathbf{M}$ of a certain region points in the same direction as the local $\mathbf{B}$ -field it produces, which is the direction of the average magnetic dipole moment. The magnetisation field lines move from near the south pole of a magnet to near its north, and so unlike $\mathbf{B}$, $\mathbf{M}$ is divergent and only exists in the sample. The total magnetic flux density inside the sample can be related to the total current density by Ampere's law

$$\nabla \times \mathbf{B} = \mu_0 (\mathbf{J}_c + \mathbf{J}_b) \quad (2.15)$$

where $\mathbf{J}_c$ is the current due to moving charges in the sample, and μ_0 is the permeability of free space. The first term $\mathbf{J}_c$, can be measured, but the bound current $\mathbf{J}_b$ cannot. To keep Ampere's law consistent, an auxiliary, or magnetic field, $\mathbf{H}$, is defined as

$$\mathbf{H} = \mathbf{B}/\mu_0 - \mathbf{M} \quad \text{or} \quad \mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M}) \quad (2.16)$$

where μ_0 is the permeability of free space, and $\mathbf{M}$ is the volume magnetisation. Inspecting (2.15) and (2.13) we can see that

$$\nabla \times \mathbf{H} = \mathbf{J}_c \quad (2.17)$$

The magnetic flux density $\mathbf{B}$ does not distinguish between external free currents, and the internal bound currents (equation 2.15), in both cases it forms loops around the currents (equation 2.15). In contrast, the magnetic field $\mathbf{H}$ treats free and bound currents differently. Ampere's law tells us that the $\mathbf{H}$ -field loops around free currents

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(equation 2.17), or in integral form using Stokes' theorem:

$$\oint_L \mathbf{H} \cdot d\mathbf{l} = \oint_L (\mathbf{B}/\mu_0 - \mathbf{M}) \cdot d\mathbf{l} = \oint_S \nabla \times (\mathbf{B}/\mu - \mathbf{M}) \cdot d\mathbf{A} = I_{tot} - I_b = I_c \quad (2.18)$$

and using Gauss's theorem, we can see that a surface integral of $\mathbf{H}$ over any closed surface is independent of the free currents and only results in a magnetic charge $q_m = -\nabla \cdot \mathbf{M}$

$$\oint_S \mu_0 \mathbf{H} \cdot d\mathbf{A} = \oint_S (\mathbf{B} - \mu_0 \mathbf{M}) \cdot d\mathbf{A} = 0 - \mu_0 \oint_V \nabla \cdot \mathbf{M} \cdot dV = \oint_V q_m \cdot dV \quad (2.19)$$

In the absence of an external magnetic field, and current the $\mathbf{H}$ -field lines are identical to $\mathbf{B}$ -field lines outside a magnet (the stray field), and only differ by a factor μ_0 , ($\mathbf{B} = \mu_0 \mathbf{H}$); but inside they can point in different directions (the demagnetising field $\mathbf{H}_d$), depending on the value of the magnetisation $\mathbf{M}$. $\mathbf{B}$ is solenoidal ($\nabla \cdot \mathbf{B} = 0$), meaning that its field lines either always form closed loops, or extend to infinity, whereas $\mathbf{H}$ is conservative and irrotational ($\nabla \times \mathbf{H} = 0$). $\mathbf{H}$ has non-zero divergence, and has sources and sinks similar to the electric field $\mathbf{E}$.

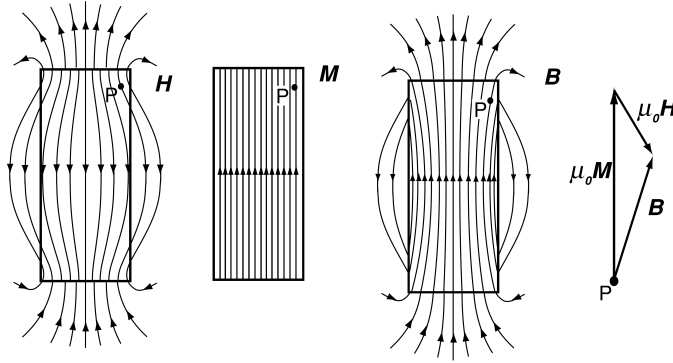


Figure 2.2: $\mathbf{H}$, $\mathbf{M}$ and $\mathbf{B}$ fields for a uniformly magnetised material in the absence of an external magnetic field [2].

Thus analogous to the electric field $\mathbf{E}$, the source of the $\mathbf{H}$ -field can be modelled as fictitious surface charges $q_m = -\nabla \cdot \mathbf{M}$, which is another way of saying the source of $\mathbf{H}$ is the non-uniformity of $\mathbf{M}$. This approach can be a convenient method to calculate external magnetic fields from permanent magnets. However, the downside is that this model fails to predict the magnetic fields inside ferromagnetic material correctly. This method will be discussed in §4.3.

Generally the $\mathbf{H}$ -field inside a uniformly magnetised body is not uniform, however for quadratic surfaces (such as hyperboloids or paraboloids) the internal field is uniform. Normally this is stated to be true for only ellipsoids, as the other surface types extend to infinity and are not so useful or convenient in three dimensions. If an ellipsoid is uniformly magnetised in the absence of external fields the internal, or demagnetising field is

$$\mathbf{H}_d = -\mathbf{NM} \quad (2.20)$$

where $\mathcal{N}$ is the demagnetising factor. The demagnetising factor $\mathcal{N}$ is a symmetric 3×3 tensor with trace 1, and is normally defined for a co-ordinate system in which it is diagonal; e.g. for a sphere, which has equal axes, the diagonals have values of $N_x = N_y = N_z = 1/3$. The demagnetising field is a convenience used to represent the internal $\mathbf{H}$ -field decrease due to the minimisation of the total energy in a magnet by its shape anisotropy energy. The shape anisotropy, or magnetostatic self-energy of a uniformly magnetised ellipsoid, or more generally, a uniformly magnetised arbitrary volume rotated to diagonalise the demagnetising tensor is

$$E_M = \frac{1}{2} \mu_0 (N_x M_x^2 + N_y M_y^2 + N_z M_z^2) V \quad (2.21)$$

What this says is that the magnetostatic self-energy of any volume (including ones with cavities) behaves like that of an ellipsoid, if and only if the volume is uniformly magnetised. For example, a uniformly magnetised cube should have the same demagnetising tensor as a sphere if it is uniformly magnetised. With a sufficiently large external field it is possible to bring the magnetisation of the cube close to uniformity, but it requires a complicated, non-uniform external field to make it fully uniform. Therefore in practical terms, the use of the demagnetising tensor is an approximation. Nonetheless, it is a useful approximation, as it allows the intrinsic magnetic properties of a sample to be studied.

The response of a linear, homogeneous and isotropic medium (i.e. its magnetisation $\mathbf{M}$) to an externally applied magnetic field $\mathbf{H}'$ is a constant known as the magnetic susceptibility:

$$\chi' = \mathbf{M}/\mathbf{H}' \quad (2.22)$$

and following in the same vein as the demagnetising field discussion, the response of the magnetisation to the internal field $\mathbf{H}$, the internal susceptibility χ is

$$\chi = \mathbf{M}/\mathbf{H} \quad (2.23)$$

The two susceptibilities are related by

$$1/\chi = 1/\chi' - \mathcal{N} \quad (2.24)$$

The dimensionless susceptibility, χ , is typically small in electrochemical systems (10^{-5} – 10^{-2}) and the difference between χ' and χ , due to the demagnetising field $\mathbf{H}_d$, can be ignored.

For solutions used in electrochemistry, the susceptibility can be written as the sum of the susceptibility of water and ions in solution

$$\chi = \chi^{\text{water}} + \chi_m c \quad (2.25)$$

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where $\chi^{\text{water}} = -9 \cdot 10^{-6}$, χ_m is the molar susceptibility and c is the molar concentration of ions in solution.

Tables 2.1 and 2.2 show the calculated and measured magnetic moments for 3d and 4f ions assuming total angular momentum, and spin-only moments. Interestingly for 3d ions in compounds, S is the good quantum number for predicting the ion magnetic moment, giving values close to measured values. For this to occur the orbital angular momentum L must be quenched. This situation arises in crystals, where the crystal field generates a non-central electric field that causes the plane of orbit to move. This means that the time averaged orbital angular momentum is zero. Conversely for 4f ions the total angular momentum J is the correct quantum number to use. The spin-orbit coupling in 4f ions is much larger compared to that of the 3d ions (approx. twice as large), and their crystal fields are 3 to 10 times smaller [3], so the crystal field quenching is not as effective in 4f ions.

Solutions containing paramagnetic 3d ions have been measured extensively since the late 19th century, and since then the ion moments have been shown to agree with the spin-only moments of ions in crystal lattices rather than free ions, and are independent of concentration [4–9]. Initially this may seem like a strange result, since the ions are fully dissolved and assumed to act as free ions in solution. However, this ignores any interaction between the water molecules and the ions. Due to the electronegativity of oxygen in water molecules, a solvation shell forms around each ion, and for 3d ions $X_6(\text{H}_2\text{O})$ complexes are formed [10], meaning the ion sits at an octahedral site, and the crystal field quenches L .

The molar susceptibility of non-interacting spin-only ions is given by the Curie law [2] (see table 2.1)

$$\chi_m = \frac{\mu_0 N_A g^2 \mu_B^2 S(S+1)}{3k_B T} \quad (2.26)$$

where N_A is Avogadro's number, g is the g factor ($= 2$ for a spin only moment), μ_B is the Bohr magneton, S is the ion spin angular momentum, and k_B is Boltzmann's constant. This can be rewritten as

$$\chi_m = \frac{1.571 \cdot 10^{-6} p_{eff}^2}{T} \quad (2.27)$$

Table 2.1: Molar susceptibility and 1 molar solution susceptibility for selected paramagnetic 3d ions (adapted from [11]).

$3d^n$	Ion	S	L	J	g_J	p_{eff}^J	p_{eff}^S	p_{eff}^{exp}	χ_m^{exp} $\times 10^{-9}$ ($\text{m}^3 \text{mol}^{-1}$)	χ_{soln}^{exp} $\times 10^{-6}$ (1 mol)
1	Ti ³⁺ , V ⁴⁺	1/2	2	3/2	4/5	1.55	1.73	1.7	15.2	6.2
2	Ti ²⁺ , V ³⁺	1	3	2	2/3	1.63	2.83	2.8	41.3	32.3
3	V ²⁺ , Cr ³⁺	3/2	3	3/2	2/5	0.78	3.87	3.8	76.1	67.1
4	Cr ²⁺ , Mn ³⁺	2	2	0	0	-	4.9	4.9	126.6	126.6
5	Mn ²⁺ , Fe ³⁺	5/2	0	5/2	2	5.92	5.92	5.9	183.5	174.5
6	Fe ²⁺ , Co ³⁺	2	2	4	3/2	6.71	4.9	5.4	153.7	144.7
7	Co ²⁺ , Ni ³⁺	3/2	3	9/2	4/3	6.63	3.87	4.8	121.5	112.4
8	Ni ²⁺	1	3	4	5/4	5.59	2.83	3.2	54.0	44.9
9	Cu ²⁺	1/2	2	5/2	6/5	3.55	1.73	1.9	19.0	10.0

Table 2.2: Molar susceptibility and 1 molar solution susceptibility for selected paramagnetic 4f ions. Note the susceptibilities are tabulated in units one order of magnitude larger than those of the 3d ions (adapted from [11]).

$4f^n$	ion	S	L	J	g_J	p_0	p_{eff}	p_{eff}^{exp}	χ_m^{exp} $\times 10^{-8}$ ($\text{m}^3 \text{mol}^{-1}$)	χ_{soln}^{exp} $\times 10^{-5}$ (1 mol)
1	Ce ³⁺	1/2	3	5/2	6/7	2.14	2.54	2.5	3.29	2.39
2	Pr ³⁺	1	5	4	4/5	3.2	3.58	3.5	6.46	5.55
3	Nd ³⁺	3/2	6	9/2	8/11	3.27	3.52	3.4	6.09	5.19
4	Pm ³⁺	2	6	4	3/5	2.4	2.68	-	-	-
5	Sm ³⁺	5/2	5	5/2	2/7	0.71	0.85	1.7	1.52	0.62
6	Eu ³⁺	3	3	0	0	0	0	3.4	6.09	5.189
7	Gd ³⁺	7/2	0	7/2	2	7	7.94	8.9	41.76	40.85
8	Tb ³⁺	3	3	6	3/2	9	9.72	9.8	50.63	49.73
9	Dy ³⁺	5/2	5	15/2	4/3	10	10.65	10.6	59.23	58.33
10	Ho ³⁺	2	6	8	5/4	10	10.61	10.4	57.02	56.11
11	Er ³⁺	3/2	6	15/2	6/5	9	9.58	9.5	47.58	46.67
12	Tm ³⁺	1	5	6	7/6	7	7.56	7.6	30.45	29.54
13	Yb ³⁺	1/2	3	7/2	8/7	4	4.53	4.5	10.68	9.77

2.2 Magnetohydrodynamics

Before discussing magnetic forces in an electrochemical cell it is important to list the governing equations of MHD, which consist of a reduced form of Maxwell's equations and Newton's second law:

(i) Ampere's law plus charge conservation

$$\nabla \times \mathbf{B} = \mu \mathbf{J} \quad (2.28)$$

$$\nabla \cdot \mathbf{J} = 0 \quad (2.29)$$

(ii) Faraday's law plus the solenoidal constraint of $\mathbf{B}$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad (2.30)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (2.31)$$

$$(2.32)$$

(iii) Ohm's law plus the Lorentz force for charges moving at a velocity $\mathbf{v}$

$$\mathbf{J} = \sigma(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad (2.33)$$

$$\mathbf{F} = \mathbf{J} \times \mathbf{B} \quad (2.34)$$

(iv) which combine to give the induction equation

$$\frac{\partial \mathbf{B}}{\partial t} = \nabla \times (\mathbf{v} \times \mathbf{B}) + \lambda \nabla^2 \mathbf{B} \quad (2.35)$$

where $\lambda = (\mu\sigma)^{-1}$ is the magnetic diffusivity in ($\text{m}^2 \text{s}^{-1}$). This equation is in effect a transport equation for $\mathbf{B}$, if we know $\mathbf{v}$ then we can predict the spatial and temporal evolution of $\mathbf{B}$.

From Newton's second law we get the Navier-Stokes equation for MHD

$$\frac{D\mathbf{v}}{Dt} = -\nabla(p/\rho) + \nu \nabla^2 \mathbf{v} + (\mathbf{J} \times \mathbf{B})/\rho \quad (2.36)$$

where ν is the kinematic viscosity, and is related to the dynamic viscosity, η by $\nu = \eta/\rho$. Da/Dt is the substantive, or convective derivative; it represents the rate of change of quantity, $\mathbf{a}$, associated with a fluid element. It is defined as

$$\frac{D}{Dt}(\mathbf{a}) = \frac{\partial}{\partial t}(\mathbf{a}) + (\mathbf{a} \cdot \nabla)(\mathbf{a}) \quad (2.37)$$

This is quite different to $\partial \mathbf{a} / \partial t$ which is the rate of change of $\mathbf{a}$ at a fixed point in space. One example is DT/Dt which is the rate of change of temperature of a fluid element

as it moves, whereas $\partial T/\partial t$ is the rate of change of temperature at a fixed point.

(v) Finally, the induction and Navier-Stokes equations leads us to the vorticity equation

$$\frac{\partial \omega}{\partial t} = \nabla \times (\mathbf{v} \times \omega) + \nu \nabla^2 \omega + \nabla \times (\mathbf{J} \times \mathbf{B})/\rho \quad (2.38)$$

where $\omega = \nabla \times \mathbf{v}$ is the vorticity field of the fluid.

2.2.0.5 Characteristic MHD numbers

Similar to §1.5.4, where we introduced convection, and the dimensionless numbers used in fluid dynamics, there are dimensionless numbers used in magnetohydrodynamics as indicators of the relative interaction strengths. The first of these is the **Magnetic Reynolds number**

$$R_m = ul/\lambda = \mu \sigma ul \quad (2.39)$$

where l is a characteristic lengthscale, e.g. for a square pipe, l is the width of the pipe. In contrast to the other dimensionless numbers, the magnetic Reynolds number has nothing to do with forces, rather it is the ratio of the convection of $\mathbf{B}$ to the diffusion of $\mathbf{B}$. It can also be viewed as a measure of the dimensionless conductivity. When R_m is large, diffusion is weak, and the magnetic field lines act like elastic bands frozen into the conducting medium due to maxwell stresses (see §2.6). This is the case, for example in interstellar media such as astrophysical plasma. In aqueous solutions, which are poor conductors, R_m is small and the induced field is negligible compared to the imposed field. The magnetic field behaviour is quite different to high R_m systems, the magnetic interaction becomes dissipative rather than elastic; Ohm's law and the Lorentz force simplify to

$$\mathbf{J} = \sigma [-\nabla V + \mathbf{v} \times \mathbf{B}] \quad (2.40)$$

$$\mathbf{F} = \mathbf{J} \times \mathbf{B} \quad (2.41)$$

where V is the electrostatic potential. The second commonly used dimensionless number is called the **Interaction parameter**

$$N_m = \sigma B^2 l / \rho u = l / u \tau \quad (2.42)$$

where $\tau = (\sigma B^2 / \rho)^{-1}$ is the magnetic damping time. The interaction parameter is the ratio of Lorentz forces to inertia. Finally, there is the **Hartmann number**

$$Ha = \sqrt{N_m Re} = Bl \sqrt{\sigma / \rho \nu} \quad (2.43)$$

The Hartmann number squared (Ha^2) represents the ratio of Lorentz forces to shear forces.

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Table 2.3: Typical forces, and estimate values, in a magneto-electrochemical cell.

Force	Expression	Typical Value ^a (N m ⁻³)
Diffusion	$RT\nabla c$	10^{10}
Migration	$zFc\nabla V$	10^{10}
Forced convection at an RDE	$\rho(r\omega)^2/2\delta_0$	10^5
Natural convection	$\Delta\rho\mathbf{g}$	10^2
Viscous drag	$\rho\nu\nabla^2 v$	10^2
Field gradient force	$\mu_0\chi cH\nabla H$	10^2
Lorentz force	$\mathbf{J} \times \mathbf{B}$	10^3
Amperian attraction	$(\mu_0/4\pi r^2)\mathbf{I}_1\mathbf{I}_2u_T^2u_n$	10^{-5}
Magnetic damping force	$\sigma(\mathbf{v} \times \mathbf{B}) \times \mathbf{B}$	10^1

^a Calculated for $T = 298$ K, $c = 10^3$ mol m⁻³, $\delta = 10^{-4}$ m, $z = 1$, $V = 1$ V, $\rho = 10^3$ kg m⁻³, $d = 10^{-2}$ m, $\omega = 10^2$ rad s⁻¹, $\Delta\rho = 10$ kg m⁻³, $\eta = 10^{-3}$ N s m⁻², $v = 10^{-1}$ m s⁻¹, $B = 1$ T, $\chi_m = 10^{-8}$ m³ mol⁻¹, $\nabla B = 10$ T m⁻¹, $j = 10^3$ A m⁻², and $\sigma = 10^2$ Ω⁻¹ m⁻¹

2.3 Ampèrian Contraction

Even with no external field there is an attractive force between moving charges, described by Ampère's force. For pairs of current elements the elemental force $\delta F_{m,n}$ is [12]

$$\delta^2 F_{1,2} = -\frac{\mu_0 I_1 I_2}{4\pi r^2} \hat{\mathbf{r}} (2 \, ds_1 \cdot ds_2 - 3 \, ds_1 \cdot \hat{\mathbf{r}} \, ds_2 \cdot \hat{\mathbf{r}}) \quad (2.44a)$$

$$\text{or} = \frac{\mu_0}{4\pi r^2} I_1 I_2 \, ds_2 \times (ds_1 \times \hat{\mathbf{r}}) \quad (2.44b)$$

where I_1 and I_2 are the currents flowing in the current elements of length ds_1 and ds_2 respectively, $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ is the distance between the centres of the two elements, and $\hat{\mathbf{r}} = \mathbf{r}/r$. Typical currents for the electroreduction of nitrobenzene (see §5.2.1) at a disc electrode of diameter 0.5 mm, are $\sim 10^{-4}$ A, i.e. $J \sim 10^2$ A m⁻² and the transverse, attractive body force is $\sim 10^{-5}$ N m⁻³. For the electrochemical systems studied here, this force is too small to have a measurable effect (see table 2.3).

2.4 Magnetic forces in a uniform magnetic field

2.4.1 In the absence of currents

In a uniform magnetic field, $\mathbf{H}'$, the force density acting on a non-uniformly magnetised material in the absence of currents can be represented by a distribution of fictitious magnetic charges, $q_m = -\nabla \cdot \mathbf{M}$, and is $\mathbf{F} = -\mu_0(\nabla \cdot \mathbf{M})\mathbf{H}'$. This arises from the force a single magnetic charge experiences in a magnetic field $\mathbf{f} = \mu_0 q_m \mathbf{H}'$. Recalling that

$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})$ and $\nabla \cdot \mathbf{B} = 0$ leads to

$$\begin{aligned} 0 &= \nabla \cdot (\mathbf{H} + \mathbf{M}) \\ \nabla \cdot \mathbf{H} &= -\nabla \cdot \mathbf{M} \\ \therefore \mathbf{F} &= \mu_0(\nabla \cdot \mathbf{H})\mathbf{H}' & (2.45) \\ &= \mu_0[\nabla \cdot (\mathbf{H}' + \mathbf{H}_d)]\mathbf{H}' & (2.46) \end{aligned}$$

where $\mathbf{H}_d$ is the demagnetising field. However, the applied field $\mathbf{H}'$ is uniform, and as long as the demagnetising field is negligible there is no net force. This is true for electrochemical systems as the demagnetising field is indeed negligible.

2.4.2 Lorentz force

2.4.2.1 Convective Effects

In aqueous solutions, moving charges interact with a magnetic field through the Lorentz force

$$\mathbf{F}_L = \mathbf{J} \times \mathbf{B} \quad (2.47)$$

At low magnetic Reynolds numbers the Lorentz force can act both as a convective driving force, and a dissipative force, converting kinetic energy to Joule heating [13]. Acting as a driving force, the Lorentz force can induce convection in a bulk solution [14, 15]. For the latter case, the Lorentz force is expressed as the magnetic damping force

$$\mathbf{F} = \sigma \mathbf{v} \times \mathbf{B} \times \mathbf{B} \quad (2.48)$$

which impedes any flow perpendicular to $\mathbf{B}$; this is usually negligible in aqueous solutions [16], but is important for suppressing convection in conductive melts used in steel and aluminium casting [13], and in silicon crystal growth.

2.4.2.2 Hall Effect

The Lorentz force can also influence the conductivity and diffusivity of ions through the Hall effect [17]. It was proposed as early as 1897 that the Hall effect should be measurable in liquids [18], which was confirmed over a number of experiments including those done by Oxley in 1913 using CuSO_4 , AgNO_3 and CdSO_4 solutions [19]. There have been numerous theoretical studies on the Hall effect in liquids, with most of them modelling imposed magnetic fields on rotating disc electrodes [20–25], and some more recent measurements using thermal gradient driven flows [26]. The Hall effect alters the mobility of an ion, described by the mobility tensor

$$\mathbf{u}_i = \begin{vmatrix} u_T & u_H & 0 \\ -u_H & u_T & 0 \\ 0 & 0 & u_{\parallel} \end{vmatrix} \quad (2.49)$$

where u_H , u_T and $u_{\parallel}$ are the Hall, transversal, and zero field mobilities respectively. In more detail they are

$$u_H = \frac{u^2 \Gamma B}{1 + u^2 \Gamma^2 B^2} \quad , \quad u_T = \frac{u}{1 + u^2 \Gamma^2 B^2} \quad \text{and} \quad u_{\parallel} = u \quad (2.50)$$

where Γ is a kinetic energy factor specific to the ion [17]. For a KCl solution containing $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in a 1 T field, $\Gamma \sim 10^3$ and $u \approx 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, then $u_H \approx u^2 \Gamma B$ and $u_T \approx u$. Remembering from chapter 1 that the diffusion coefficient and conductivity of an ion, i , can be related to the mobility thus

$$\kappa_i = F \Sigma_i |z_i| c_i \mathbf{u}_i \quad \text{and} \quad \mathbf{D}_i = \frac{\mathbf{u}_i R T}{z_i F} \quad (2.51)$$

which means that it is possible for them to be influenced by the magnetic field. As mentioned previously, migratory effects are normally minimised through the use of dilute solutions with a much larger concentration of supporting electrolyte, and this effect can be safely neglected [17].

2.5 Magnetic forces in a non-uniform magnetic field

The magnetostatic energy stored per unit volume (energy density) in an electrolyte in an external magnetic field is commonly given as [27]

$$E_m = \frac{1}{2} \mu_0 M H \quad \text{or} \quad = \frac{1}{2} \mu_0 \chi H^2 \quad (2.52)$$

where M is the induced magnetisation $\mathbf{M} = \chi \mathbf{H}$, and χ is the dimensionless susceptibility of the electrolyte. The 1/2 factor is a consequence of the work done in creating and maintaining the magnetisation. The force density acting on the electrolyte can be derived from the gradient of the energy density $\mathbf{F}_m = -\nabla E_m$, noting that the susceptibility is $\chi = \chi^{\text{water}} + \chi_m c$, it follows that

$$\mathbf{F}_m = \mu_0 \chi_m c H \nabla H + \frac{1}{2} \mu_0 \chi_m H^2 \nabla c \quad (2.53)$$

The first term is the field gradient force,

$$F_{\nabla H} = \mu_0 \chi_m c H \nabla H \quad (2.54)$$

and the second term has been referred to as the “magnetic concentration gradient force” or “paramagnetic force”. It is supposed to exist in a uniform magnetic field.

$$F_{\nabla C} = \frac{1}{2} \mu_0 \chi_m H^2 \nabla c \quad (2.55)$$

The field gradient force is a well known body force, whose most dramatic manifestation is in magneto-Archimedes levitation. The difference in susceptibility of an object and its environment, plus the buoyancy differences can lead to levitation in ferrofluids [28], paramagnetic liquids [29, 30], liquid oxygen [31] or directly in air [32–38]. An example of magneto-Archimedes levitation is shown in fig. 2.3. The field gradient force, like the Lorentz force is a body force acting across a volume of a solution, whereas diffusion acts on individual ions or molecules in solution. Therefore one would expect the field gradient force to influence convection and not diffusion. Taking typical values in an electrochemical cell, $\chi_m = 1.9 \cdot 10^{-8} \text{ m}^3 \text{ kg}^{-1}$, $c = 1 \text{ mol l}^{-1}$, $B = 1 \text{ T}$, and $\nabla B = 10 \text{ T m}^{-1}$, $F_{\nabla B} = 152 \text{ N m}^{-3}$ (see table 2.1), which is a moderate force density, but the energy of a Co^{2+} ion ($S = 1/2$) in a 1 T field is

$$E = \frac{\mu_0 g^2 \mu_B S(S+1) B^2}{2k_B T} = 7 \cdot 10^{-7} \text{ eV}$$

which is considerably less than the thermal energy driving diffusion ($k_B T \sim 1/40 \text{ eV}$).

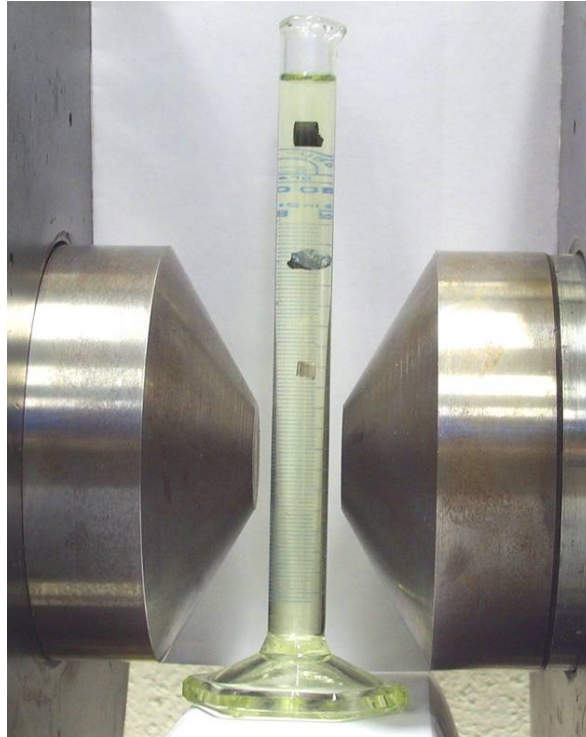


Figure 2.3: From top to bottom, C, Si, and Ti levitating in a 2.67 M $\text{Dy}(\text{NO}_3)_3$ solution in the fringing field of a 1.5 T electromagnet. [30]

The second term, the magnetic concentration gradient force, was introduced by Waskaas and Kharkats to explain magneto-convective effects in the apparent absence of Lorentz

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force effects. However, as argued by Coey *et al.* [27], this force relation arises from an incorrect formulation of the energy of a magnetic dipole in a magnetic field. A simple argument that it is not a body force as follows. Suppose there is a non-uniform concentration (fig. 2.4) in a uniform field $\mathbf{H}'$ which leads to a non-uniform magnetisation $\mathbf{M}$, as described in §2.4.1. The force on this volume is

$$\mathbf{F}_m = -\mu_0(\nabla \cdot \mathbf{M})\mathbf{H}' \quad \text{or} \quad = \mu_0[\nabla \cdot (\mathbf{H}' + \mathbf{H}_d)]\mathbf{H}' \quad (2.56)$$

Remembering that the divergence of $\mathbf{M}$ is

$$\nabla \cdot \mathbf{M} = \frac{\partial M_x}{\partial x} + \frac{\partial M_y}{\partial y} + \frac{\partial M_z}{\partial z} \quad (2.57)$$

we construct two cases, where the applied magnetic field is perpendicular, and parallel to the concentration gradient. In case 1 (fig. 2.4.a), a large external field $\mathbf{H}'$, sufficient to fully magnetise the paramagnetic volume is applied along the z-axis, perpendicular to the concentration gradient. The magnetisation $\mathbf{M}$ also lies only in the z-axis ($M_x = M_y = 0$), and is uniform along this axis ($\frac{\partial M_z}{\partial z} = 0$); therefore $\nabla \cdot \mathbf{M} = 0$ and there is no force for an applied field perpendicular to the concentration gradient. For a magnetic field applied parallel to the concentration gradient (case 2, fig. 2.4.b), we know that $\nabla \cdot \mathbf{M} = -\nabla \cdot \mathbf{H}_d$, but H_d is negligible in electrochemical cells, therefore there is no “magnetic concentration gradient force” across the interface.

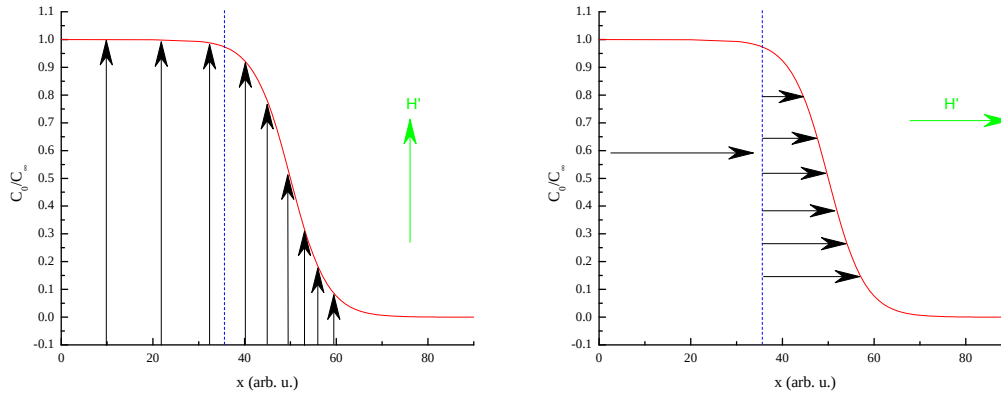


Figure 2.4: Magnetisation across a non-uniform concentration profile in an external magnetic field. Black arrows indicate magnetisation, $\mathbf{M}$ and the green arrow indicates the direction of the applied magnetic field $\mathbf{H}'$. (a) case 1 $\nabla \cdot \mathbf{M} = 0$, and (b) case 2 $\nabla \cdot \mathbf{M} = \nabla \cdot \mathbf{H}_d$

Another approach to describe the response of paramagnetic materials to a non-uniform magnetic field $\mathbf{H}'$ is to treat it as a force density acting on a uniformly magnetised distribution of magnetic dipoles $\mathbf{m}$. The energy of a magnetic dipole in a magnetic field is then [2]

$$U = \mathbf{m} \cdot \mu_0 \mathbf{H}' \quad (2.58)$$

and hence the force is $\mathbf{F} = -\nabla U = -\mu_0 \nabla(\mathbf{M} \cdot \mathbf{H})$. Using the identity

$$\nabla(\mathbf{M} \cdot \mathbf{H}) = (\mathbf{H} \cdot \nabla)\mathbf{M} + (\mathbf{M} \cdot \nabla)\mathbf{H} + \mathbf{H} \times (\nabla \times \mathbf{M}) + \mathbf{M} \times (\nabla \times \mathbf{H})$$

while also assuming $\mathbf{M}$ is uniform and independent of $\mathbf{H}'$ ($\nabla \times \mathbf{M} = 0$), and that there are no currents ($\nabla \times \mathbf{H}' = 0$) this simplifies to the Kelvin force

$$\mathbf{F} = \mu_0(\mathbf{M} \cdot \nabla)\mathbf{H}' \quad (2.59)$$

It must be noted that the Kelvin force is only valid for linear media where the susceptibility is linear in density, i.e. $\chi = \alpha\rho$ where α is a proportionality constant [40], and where we have assumed ($\nabla \times \mathbf{M} = 0$). This is not true for ferrofluids; the correct description of the force in the absence of currents is the Helmholtz force rather than the Kelvin force [41, p. 127] (see appendix A for derivation)

$$\mathbf{F} = \frac{\mu_0}{2} \nabla \left[H'^2 \rho \left(\frac{\partial \chi}{\partial \rho} \right)_{T,P} \right] - \frac{\mu_0}{2} H'^2 \nabla \chi \quad (2.60)$$

In this formulation, there is a concentration gradient force, but it is only a higher order correction term to the force density. In linear, isotropic media, the susceptibility is proportional to the density, $\rho(\partial\chi/\partial\rho) = \chi$, and the Helmholtz force reduces to the Kelvin force $\mathbf{F} = (\mu_0/2)\chi\nabla H'^2 = \mu_0\mathbf{M}\nabla\mathbf{H}'$; meaning there is no concentration gradient force in dilute systems such as electrochemical systems. The significance of this will be discussed in §2.7.

2.6 Maxwell stresses

From Ampere's law we may rewrite the Lorentz force in terms of $\mathbf{B}$ alone. Starting with the vector identity

$$\nabla(\mathbf{B}^2/2) = (\mathbf{B} \cdot \nabla)\mathbf{B} + \mathbf{B} \times \nabla \times \mathbf{B}$$

and using $\nabla \times \mathbf{B} = \mu\mathbf{J}$ we arrive at

$$\mathbf{J} \times \mathbf{B} = (\mathbf{B} \cdot \nabla)(\mathbf{B}/\mu) - \nabla(\mathbf{B}^2/2\mu) \quad (2.61)$$

This can also be written as

$$\mathbf{J} \times \mathbf{B} = \frac{\partial}{\partial s} \left[\frac{B^2}{2\mu} \right] \hat{\mathbf{e}}_t - \frac{B^2}{\mu R} \hat{\mathbf{e}}_n - \nabla(B^2/2\mu) \quad (2.62)$$

where $\hat{\mathbf{e}}_t$ and $\hat{\mathbf{e}}_n$ represent unit vectors tangential and normal to the field line, and ∂s is the surface element of a field line. The second term on the right, $-\nabla(\mathbf{B}^2/2\mu)$, acts on the fluid in the same way as the pressure force $-\nabla p$. It is irrotational, and so

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does not appear in the vorticity equation; meaning that it cannot influence the flow field. In flows without a free surface (i.e. wall boundaries in all directions) it acts as an additional pressure, and is commonly referred to as magnetic pressure term. In many cases it can be insignificant to the dynamics of a system [13]. When the magnetic Reynolds number is large (such as in liquid metal flows or plasmas) the magnetic pressure becomes important, in some cases causing oscillations (Alfvén waves) in the fluid [13]. However, in the presence of a uniform magnetic field the magnetic tension and pressure are not observed. A more complete description of the Maxwell stresses is encompassed in the the Maxwell stress tensor which treats the interaction of the electric and magnetic fields, and the resultant body force as a surface stress

$$T_{ij} = \epsilon_r \epsilon_0 E_i E_j + \frac{1}{\mu} B_i B_j - \frac{1}{2} \left(\epsilon_r \epsilon_0 E^2 + \frac{1}{\mu} B^2 \right) \delta_{ij} \quad (2.63)$$

where ϵ_0 is the permittivity of free space and δ_{ij} is Kronecker's delta. In the presence of only a $\mathbf{B}$ -field this simplifies to

$$\sigma_{ij} = \frac{1}{\mu_0} B_i B_j - \frac{1}{2\mu_0} B^2 \delta_{ij} \quad (2.64)$$

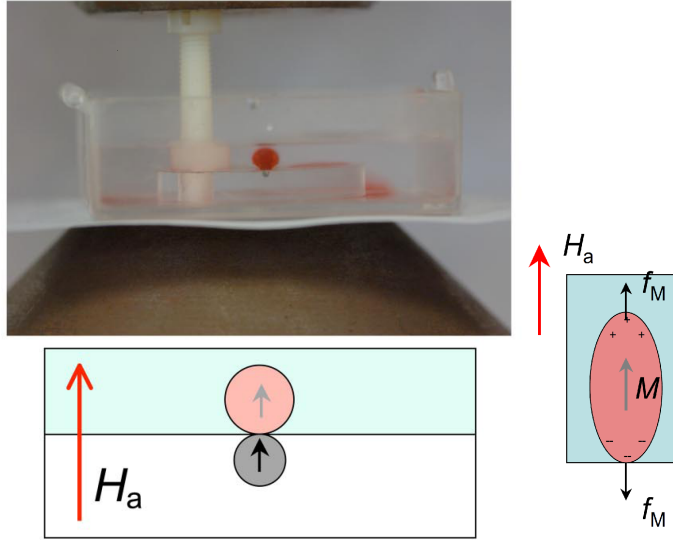


Figure 2.5: Maxwell stress on a magnetic field gradient-confined paramagnetic liquid tube [42]: 1 M ErCl_3 injected into DI water forms a tube above a iron wire magnetised in a 1 T vertical magnetic field due to the field gradient force, and the Maxwell stresses deform the tube in an oblate fashion.

Equations (2.61) and (2.62) are two formulations of the same phenomenon. Using the description of (2.61) rather than (2.62), the first term appears as the result of tensile stresses $\mathbf{B}^2/\mu$ on both ends of a flux tube. This corresponds to the image charge model of the $\mathbf{H}$ -field, where the force on a magnetic charge q_m is $\mathbf{f} = \mu_0 q_m \mathbf{H}$ [27]. The second interpretation, (2.62), is of two forces acting tangential and normal to a field line at every point; both interpretations are equivalent [13].

2.7 Magnetic field effects in electrochemistry

Faraday’s famous failed experiment in 1832 is considered to be the first attempt to measure an effect from what would become known as the field of magnetohydrodynamics (MHD). He tried to measure the potential difference across the Thames induced by its motion through the Earth’s magnetic field; but his equipment was not sensitive enough and the river bed short circuited the signal [13]. As far back as 1885, a magnetic field was shown to influence the corrosion of an iron electrode [43], only recently explained in terms of MHD effects [44–46]. It was not until the 1930s that MHD-like effects were studied again by Hartmann and Lazarus in liquid metals [47]. Then in 1947, Alfvén coined the term *magnetohydrodynamics* and a new field was born [13]. Progress in magneto-electrochemistry was sporadic before the 1970s. The earliest example is the study carried out by Yang in 1954 [48], who observed an increased roughness of iron, nickel, and cobalt deposits following polishing ridges of the cathode. He attributed the effect to concentration of magnetic field lines close to the protruding ridges of the substrate, creating a magnetic field gradient, which then acted to attract the paramagnetic ions. Aogaki *et al.* analytically derived a set of equations relating the limiting current to applied magnetic field for the system shown in fig. 2.6 [14, 15]. The Aogaki cell consists of two parallel plate electrodes embedded in the wall of a tube, with a perpendicular applied magnetic field which induces a flow in the tube. The limiting current densities are described by

$$j_l = j_0 + \alpha B^\beta c_0^\gamma \quad (2.65)$$

where j_0 is the zero field current density, c_0 is the ion concentration, α is a constant that depends on the cell configuration, and β and γ are indices dependent on the flow profile of the cell. For a narrow channel in a fully developed flow $\beta = 1/2$ $\gamma = 3/2$, whereas $\beta = 1/3$ $\gamma = 4/3$ for a wide channel. A similar relationship was found by Aaboubi and co workers for the $[\text{Fe}(\text{CN})_6]^{-3/-4}$ redox couple [17], and has been validated by FEM simulations [49, 50]

Previously MHD effects in solution were observed to have a dominant role and were the focus of a number of reviews, which mostly concentrate on either deposition or dissolution of metals [52–54]. During metal electrodeposition, applied magnetic fields have been shown to influence the surface morphology [48, 52–62, 62–72], crystal structure and orientation [58, 73–77], deposition rate [16, 59–61, 63, 67, 78–86], alloy composition [66, 87] and magnetic properties [58, 66, 88]. Aogaki formulated a theory describing MHD flows *inside* the diffusion layer, referred to as the micro-MHD effect [89]. Originally the theory was developed to account for copper corrosion patterns and behaviour [89–92], but now it has been used to investigate the origin of copper nodules, “magnetic micro-mystery circles” and vortex chirality observed by Aogaki during copper deposition [93, 94]. Other experimental evidence for the micro-MHD effect include the

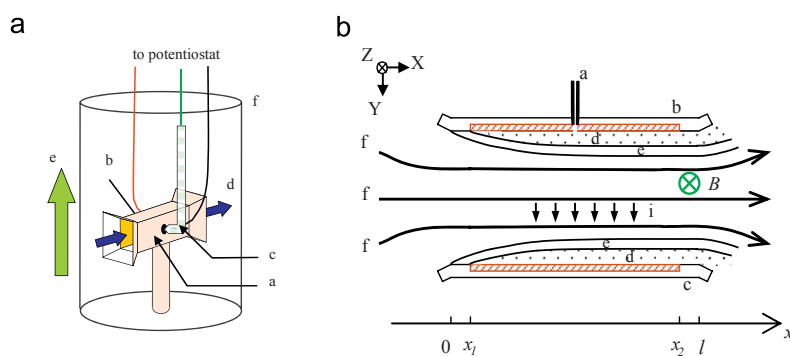


Figure 2.6: The Aogaki cell [51], (a) Schematic configuration; a: working electrode, b: counter electrode, c: Luggin capillary, d: solution flow, e: magnetic field, and f: vessel filled with solution. (b) MHD main flow and boundary layers; a: Luggin capillary, b: working electrode, c: counter electrode, d: diffusion layer, e: hydrodynamic boundary layer, and f: streamlines.

modification of fractal geometry of Zn and Cu deposits [16, 55, 62, 95], and in the morphology of Cu, Co, CoNiP, Ag, and Zn thin films. [67, 70, 74, 96, 97]. Two key features of micro-MHD flows are the asymmetric and symmetric concentration fluctuations close to the electrode surface [98]. Asymmetric fluctuations are triggered in the double layer, and determine the reaction rate, yielding 2D nuclei, and symmetric fluctuations are triggered in the diffusion layer, determining the reaction rate of each crystal/grain, and forming 3D nuclei.

Systematic studies of MHD effects on organic compounds have been carried out by Leventis, showing a very clear MHD effect using electromagnets and permanent magnets [99]. Aogaki *et al.* probed the reduction of paramagnetic oxygen in comparison to diamagnetic Ferrocene and 2,2,6,6-tetramethylpiperidiny-1-oxyl (TEMPO) in a 7 T superconducting magnet. They concluded that the electrode reaction of paramagnetic substances influenced by magnetic convection caused by a magnetic field gradient and its magnetic susceptibility; and observed only a small influence of the cyclic voltammograms of diamagnetic ferrocene [100]. Lee *et al.* used neutral molecules to probe the effect of the Lorentz force on the products, and supporting electrolyte, they showed that the limiting current is dependent on the concentration of the reactants and products close to the electrode. Under increasing magnetic fields $\text{NB}^{\bullet-}$ is swept away from the electrode, being replaced by NB, thereby increasing the limiting current [101]. Following this they studied the effect of the magnetic field gradient force in the fringing field of a superconducting magnet, with the electrode orientated to minimise Lorentz force stirring [102]. They were able to correlate current enhancements to the magnetic field gradient force demonstrating that the Lorentz force and field gradient force can be of the same order of magnitude. Henry White's group then used Fe and Pt electrodes during the reduction of nitrobenzene to differentiate the local effects due to the magnetic field gradient, and the Lorentz force [103]. At Fe electrodes they observed a focussing of the reduced species $\text{NB}^{\bullet-}$, due to the magnetic field gradient at the electrode surface

[103, 104] and modelled this successfully using the finite element method [105]. They then went on to demonstrate a microfluidic system based on focussing $\text{NB}^{\bullet-}$ at closely spaced electrodes using the Lorentz force [106]. A number of other groups have focused on using magnetic fields and field gradients to realise novel microfluidic devices, ranging from paramagnetic liquid tubes with unusual near-frictionless flows generated in bulk solutions using tailored magnetic field gradients [42, 98, 107], field gradient separation and filtration devices [108, 109] to more typical lab-on-a-chip devices using the MHD effect to pump, stir and concentrate solutions [49, 110–116].

As stated earlier, the concentration gradient force was introduced to explain magneto-convective effects in apparently zero Lorentz force systems. This formulation was a consequence of the studies on the origin and mechanism of magnetically induced rest potential shifts in equilibrium or corroding systems; which for a number of years was unknown. In fact until recently it was assumed that only ferromagnetic electrodes exhibited a rest potential shift [45]. Kelly *et al.* proposed a magnetic field induced potential difference which modified the Butler-Volmer equations and hence the kinetics of his corrosion system [117]; Perov *et al.* observed a rest potential shift for Fe but not for Co or Ni and based their explanation on stray fields created by domain walls [118, 119]. Mogi surmised a global MHD/Lorentz force stirring effect on Fe corrosion, preventing complete passivation of the electrode above 1.7 T [120]. Early on in the midst of this flowering of ideas Waskaas and Kharkats introduced a concentration gradient force to explain magnetically enhanced diffusion through a membrane [121]. They reported anodic shifts for iron in a variety of different electrolytes, the largest was 45 mV in 1 M FeCl_3 in 0.8 T. However they observed no effects for diamagnetic electrolytes such as MgCl_2 or ZnCl_2 , or for non-ferromagnetic electrodes such as copper and zinc [39, 121, 122]. It was this that led them to conclude that the effect could only be observed in ferromagnetic electrodes in paramagnetic solutions. Since then the concentration gradient force has been invoked to explain numerous phenomena in magneto-electrochemistry [84, 123–126]. It is only in the last number of years that Rhen *et al.* have established that the rest potential shift during metal corrosion is due to micro-MHD effects acting on the local currents; and does not require the electrode to be ferromagnetic, as indicated by the rest potential shifts for diamagnetic as well as paramagnetic and ferromagnetic electrodes [44, 45, 127, 128].

The invocation of the ‘concentration gradient force’ was a result of simplifications used in analysing electrochemical cells. Lorentz force flows are complicated, and three dimensional in nature [111, 130–132], even for apparently aligned systems, where B is perpendicular to the surface, edge effects generate vortices at the electrode surface [105, 106, 129, 133, 134] (see fig. 2.8), and natural convection must also be taken into account [52, 67, 126]. Neglecting these effects has lead some researchers to assume there were no Lorentz force effects when the magnetic field is perpendicular to the surface of the electrode, and to claim that $F_{\nabla C}$ could support a paramagnetic liquid

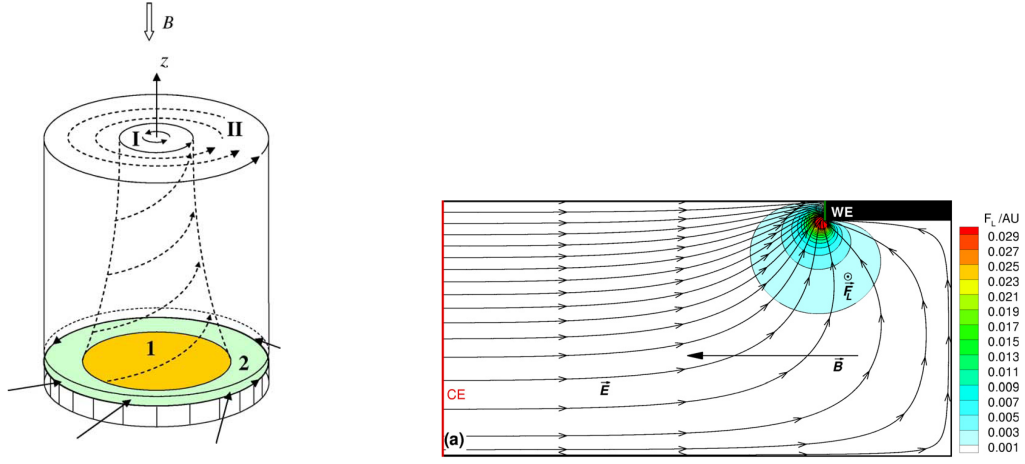


Figure 2.7: (a) Induced vortex flow due to edge currents, initially only region 2 rotates, but as the magnetic field increases, its momentum becomes enough to rotate region 1 too [129] and (b) Lorentz force distribution due to a homogeneous magnetic field and radial currents near a working electrode [130].

against gravity in the diffusion layer [135] or generate a vortex flow at an electrode in a “zero” Lorentz force configuration [136, 137]. Indeed, for simplistic analyses, where the Lorentz force is neglected, there must be some driving force, resulting in the observed phenomena; and therein lies the problem – attributing phenomena to a non-physical force while ignoring effects from well known sources. A good example of the dangers of simplification is comparing the magnetic damping of a two dimensional jet, and a three dimensional one. For both a 2D jet and a 3D jet, the Lorentz force per unit mass acting on the jet is

$$\mathbf{F} = (\mathbf{J} \times \mathbf{B})/\rho = -\mathbf{v}_\perp/\tau - \nabla V \times (\sigma \mathbf{B}/\rho) \quad (2.66)$$

where $\mathbf{v}_\perp$ is the velocity normal to $\mathbf{B}$, τ is the magnetic damping time $\tau = (\sigma B^2/\rho)^{-1}$, and ∇V is the electric field. Two important points can be made from inspecting this, first, each fluid element decelerates on a time scale of τ :

$$\frac{D\mathbf{v}_\perp}{Dt} \sim \frac{\mathbf{v}_\perp}{\tau} \quad \text{and} \quad \frac{D\mathbf{v}_\parallel}{Dt} \sim 0$$

and secondly, when an fluid element attempts to cross a field line, it experiences a frictional drag. Here we assume a simple 2D jet, $\mathbf{v}(x, y) = (v_x, v_y, 0)$ passing through a uniform magnetic field in the y-direction. When there is no electrostatic field imposed from boundaries the divergence of Ohm’s law gives

$$\nabla^2 V = \nabla \cdot (\mathbf{v} \times \mathbf{B}) = \mathbf{B} \cdot \boldsymbol{\omega} = 0 \quad (2.67)$$

and so with this simplification V is zero. Therefore the induced current $\mathbf{J} = \sigma \mathbf{v} \times \mathbf{B}$ is directed along the z -axis, and the Lorentz force $\mathbf{J} \times \mathbf{B} = -\sigma u_x B^2 \hat{\mathbf{e}}_x$ retards the flow.

Two more assumptions to simplify the model are, (i) the surrounding fluid is quiescent, i.e. $\nabla p = 0$ outside the jet, and (ii) its characteristic thickness, or broadening, δ , is much less than the characteristic axial length scale, l , then ∇p is also negligible inside the jet. Therefore since the pressure forces, and $\nabla V \times \mathbf{B}$ are zero, the fluid flow can be simplified to

$$\mathbf{v} \cdot \nabla v_x = -v_x/\tau \quad (2.68)$$

Solving this leads to a velocity distribution [13]

$$v_x = [U - x/\tau] \sec h^2(y/\delta) \quad (2.69)$$

where $U = v_x(0, 0)$. An immediate, and prominent result of the velocity field is that over a finite distance $L = U\tau$ the jet is annihilated. As we will see, this contrasts greatly with a more complicated 3D jet.

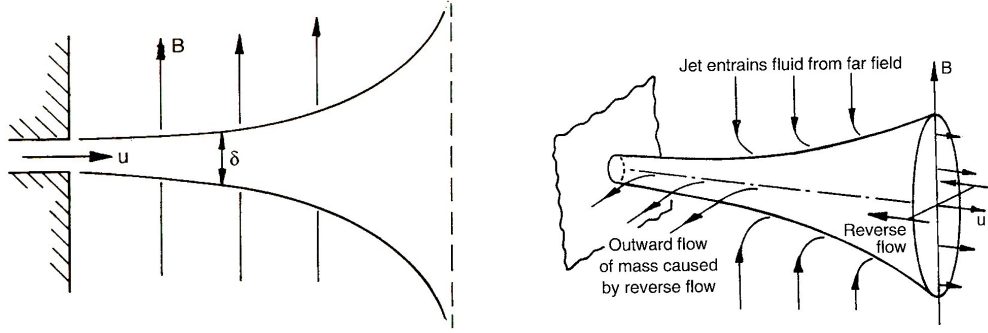


Figure 2.8: (a) Two dimensional jet in an external magnetic field, and (b) Three dimensional MHD jet [13].

Consider a unidirectional jet $\mathbf{v} = v(z, y, t)\hat{\mathbf{e}}_y$, initially symmetric across x and z , with a uniform magnetic field imposed $t = 0$ along the z -direction. Ohm's law can be reformulated as

$$\mathbf{J} = \sigma(-\nabla V + \mathbf{v} \times \mathbf{B}) \quad (2.70)$$

since $\mathbf{B}$ is uniform ($\nabla \times \mathbf{E} = 0$). Currents are induced parallel to x by $\mathbf{v} \times \mathbf{B}$, but due to the electrostatic potential, V will be forced to recirculate back through regions of weak or zero flow. This is evident from the divergence of Ohm's law, which gives $V = \nabla^{-2}(\mathbf{B}\omega)$. Since we are assuming the induced current lies only in the x - z plane, we can describe the relationship between $\mathbf{J}$ and the velocity using a streamfunction ψ . A streamfunction is a function that represents the trajectories or *streamlines* of particles in a steady flow. Streamlines are curves of the instantaneous tangent to the velocity, and so show the direction a particle or fluid element will travel at any point in time. The streamfunction for $\mathbf{J}$ is [13]

$$\mathbf{J} = \nabla \times [\psi \hat{\mathbf{e}}_y], \quad \text{and} \quad \nabla^2 \psi = -\sigma N \frac{\partial v}{\partial z} \quad (2.71)$$

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The equation of motion is therefore

$$\frac{Dv_y}{Dt} = \mathbf{v} \cdot \nabla v_y = \frac{B}{\rho} \frac{\partial \psi}{\partial z} = -\frac{1}{\tau} \nabla^{-2} \left[\frac{\partial^2 v_y}{\partial z^2} \right] \quad (2.72)$$

In low magnetic Reynolds number flows it is important to remember that while the Lorentz force is dissipative in nature, i.e. converts mechanical energy into thermal energy, momentum is conserved, which is another way of saying $\partial \psi / \partial z$ integrates to zero. This time, δ is the thickness of the jet in the x -direction, and $l_{\parallel}$ is the characteristic lengthscale for v parallel to $\mathbf{B}$. As mentioned previously, in low R_m systems the Lorentz force creates Joule heating/dissipation, and the energy dissipation can be described by [138]

$$\frac{d}{dy} \int \left(\frac{1}{2} v_y^3 \right) dA = -\frac{1}{\rho \sigma} \int \mathbf{J}^2 dA \quad (2.73)$$

from this and momentum conservation, v_y and $l_{\parallel}$ scale as [138]

$$v_y \sim \left[\frac{\tau M^2}{\delta^4 y} \right]^{1/3}, \quad \text{and} \quad l_{\parallel} \sim \left[\frac{\delta^5 y^2}{\tau^2 M} \right]^{1/3} \quad (2.74)$$

where M is the momentum flux $M = \int u_y^2 dA$. So, what we see is that the jet becomes long and elongated, which is a result of the recirculation of the induced currents; reverse flows form, and momentum diffuses out along the z -axis. Continuity of mass requires that, if the jet is to spread along the $\mathbf{B}$ -lines then some of the surrounding fluid must become entrained, i.e. have the same periodicity and vorticity. Consequently the jet draws in fluid from far-field (large $|z|$), and the reverse flows drive outward fluxes near the source of the jet.

It is obvious that the complex flows induced by the Lorentz force can only begun to be accurately described by a full three dimensional treatment. Realistic, and physical flows do not manifest themselves in simpler two-dimensional models, and simple hydrodynamic models cannot capture an accurate picture of phenomena occurring in electrochemical cells.

Supposing we do find a situation where the Lorentz force has no influence, there are still a number of compelling arguments against the existence of the concentration gradient force, $F_{\nabla c}$. Hinds *et al.* argued that that $F_{\nabla c}$ like the entropic force driving diffusion $F_D = RT \nabla c$, is proportional to, and directed along ∇c . The ratio of the two terms, $\mu_0 \chi_m H^2 / 2RT$, is of order 10^{-5} to 10^{-5} in one-molar solutions, and so they argued that it should have a negligible effect on diffusion or mass transport [16, 81]. In response, Bund claimed that $F_{\nabla c}$ is a body force which can influence convection, unlike the diffusion force which acts on individual ions or molecules creating fluxes and should not be included in the Navier-Stokes equation [126]. However as discussed in §2.5, the concentration gradient force is not a body force, and the correct description of the energy of a magnetic dipole in a magnetic field is the Helmholtz force [27]; leading

to a concentration gradient force that is only a second order correction, which is only relevant in ferrofluids and other situations where demagnetising fields are significant (see §2.5).

Finally, to date, most studies report no magnetic field effect on the kinetics of electrochemical systems [16, 139–141], only a few groups have reported kinetic changes, and none have reported a change in the double layer capacitance with magnetic field. The first report of an effect on kinetics involved the use of the Aogaki cell during copper deposition/dissolution as a hydrodynamic electrode, and under a 13 T. The exchange current was reported to decrease to 1/4 times the zero field value; no effect was seen on the charge transfer coefficient [142]. Lee *et al.* also observed a magnetic field dependent change in the kinetics during the electroless deposition of Ni onto α -Al₂O₃ [78]; and Wang *et al.* observed an increase in the charge transfer resistance for Ni/nano-Al₂O₃ composite corrosion [143].

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Chapter 3

Metal Deposition and Dissolution in Magnetic Fields

3.1 Introduction

Early on in magnetoelectrochemistry a number of questions arose based on the influence of magnetic fields on metal electrodeposition and dissolution. The magnetic field induced rest potential shift of iron has been known for well over 100 years [1], but only lately has the phenomenon been re-examined with a view to explaining how the shift in rest potential $\Delta E_0(B)$ can come about [2–8]. The direct effect of a magnetic field on the chemical potential of ferromagnetic iron is very small, amounting to only about 0.1 mV per tesla. However, shifts of up to 100 mV per tesla have been reported at very low pH, and different authors have proposed quite different origins of the effect. Similarly, in electrodeposition, the influence of magnetic fields on the hydrogen evolution reaction coupled with the metal deposition were unclear. Hinds *et al.* [9] noted from Tafel plots of copper deposition in acidified copper sulphate solution that the hydrogen and copper currents increased with applied field for overpotentials between -0.8 V and -1.5 V. However at more negative overpotentials the hydrogen current was suppressed by the magnetic field and they were unable to determine the extent of suppression. During the deposition of Ni [10], Devos *et al.* observed in electron micrographs that imposed magnetic fields distorted the formation of hydrogen bubbles at the electrode surface in a comparable way to an RDE and concluded that the observed effects were due to MHD stirring of the solution. More recently Krause *et al.* [11] and Koza *et al.* [12] both attributed an enhancement of hydrogen evolution during Fe, Co and CoFe deposition to a faster desorption of hydrogen from the electrode surface in a magnetic field. Krause *et al.* concluded that this was due to the influence of the concentration gradient force, and Koza *et al.* to stray fields in the ferromagnetic iron deposit which in turn might lead to local field gradients acting on a hydrogen bubble. However, in other papers Koza *et al.* [13, 14] attribute this enhancement to the Lorentz force. From null effects on deposition currents in the kinetically controlled deposition

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of Fe, Matsushima *et al.* concluded that the primary effects on hydrogen evolution were convection/Lorentz force related due to the hydrogen evolution reaction being mass transport limited [15]. They reported a decrease in current efficiency with applied magnetic field, as only the mass transport limited hydrogen current is enhanced, leaving little to no effect on the iron current. Further evidence to support this is in recent work by Diao *et al.* on hydrogen evolution in acidic solutions, where bubble size decreased with applied magnetic field due to MHD effects [16].

As we discussed previously, a variety of hypotheses were proposed to explain the magnetically induced rest potential shift of corroding metals. Waskaas and Kharkats [2–4] reported anodic shifts for iron in a variety of different electrolytes and the largest shift in 0.8 T was 45 mV in 1M FeCl₃, whereas they observed no effect for diamagnetic electrolytes such as MgCl₂ or ZnCl₂, or for non-ferromagnetic electrodes such as copper and zinc. These authors concluded that the effect was limited to ferromagnetic electrodes immersed in paramagnetic solutions. Their explanation was based on the concentration gradient force

$$\mathbf{F}_{\nabla c} = \frac{\chi_m B^2 \nabla c}{2\mu_0} \quad (3.1)$$

which was thought to arise when a uniform magnetic field acts on a nonuniform concentration of magnetic ions of molar susceptibility χ_m , such as exists near the electrode in the diffusion layer. Here μ_0 is the permeability of free space $4\pi \times 10^{-7} \text{ A m}^2 \text{ T}^{-1}$. However this force was discussed in §2.5, and shown to have no effect on room temperature, liquid electrochemical systems.

Perov *et al.* [6] used a differential cell with two iron electrodes connected by a salt bridge and by applying a 0.4 T magnetic field only on one electrode they observed shifts of 35 mV at in 0.16 M FeCl₃, but no effect was detected for cobalt or nickel. Their explanation involved stray fields created by domain walls in the iron [6], and they suggested the effect might be exploited as a possible magnetic field sensor [7]. Shinohara *et al.* reported anodic field induced rest potential shift of iron [5] up to 6 mV in a field of 6 T for 0.5 M NaCl solution. The shift was explained in terms of the Lorentz force

$$\mathbf{F}_L = \mathbf{j} \times \mathbf{B} \quad (3.2)$$

acting on the cathodic corrosion current via magnetohydrodynamic convection on a micron scale near the electrode, their ‘micro-MHD effect’.

The field-dependence of the effect in a variety of electrolytes was studied by Hinds *et al.* [8]. Anodic shifts of up to 35 mV in 1.4 T for 1 M Fe(NO₃)₃ were measured for Fe electrodes. Shifts of about 1 mV for cobalt and nickel were measured using an ac magnetic field, thereby overcoming the problem of the time-dependent drift in rest potential due to the aggressive electrolyte. An explanation in terms of the magnetic field gradient force

$$\mathbf{F}_{\nabla B} = \frac{\chi_m c \nabla B^2}{2\mu_0} \quad (3.3)$$

was proposed, which could act either to enhance the cathodic corrosion current or to increase the concentrations of paramagnetic ions in the vicinity of the electrode.

More recently Rhen *et al.* gave an account of the effect in zinc, which established that neither a ferromagnetic electrode nor paramagnetic ions in solution are necessary to observe the field-induced rest potential shift [17–19]. They noted that an anodic shift of the rest potential is due to an increase of the mass-transport limited cathodic corrosion current by the Lorentz force; the potential shift is needed to increase the compensating anodic current; along with the actively corroding anodic area being altered by a correlated amount [19]. The results below are a systematic study of a range of metals measured in the same conditions as in [17–19]; whose goal is to provide further support to the view that the effect is due to Lorentz force enhancement of corrosion currents - a manifestation of the micro-MHD effect.

3.2 Rest Potential Shift

3.2.1 Experimental Methods

Corrosion electrolytes containing 1 M KNO_3 , deionised water and 69 vol. % HNO_3 with a pH of 0.1 were prepared, and experiments were carried out using 30 ml fresh solutions in open atmosphere. Electrodes were prepared from 99.9 % pure foils and were polished using 400 grit sand paper prior to each experiment; and cut into 8 mm diameter discs. A Solartron model SI1280B potentiostat was used to record the rest potential as a function of time, and a 1.5 T field was applied using a 200mm electromagnet; which produces a field that is homogeneous to better than 1 part in 10^3 over the volume of the 30ml solution.

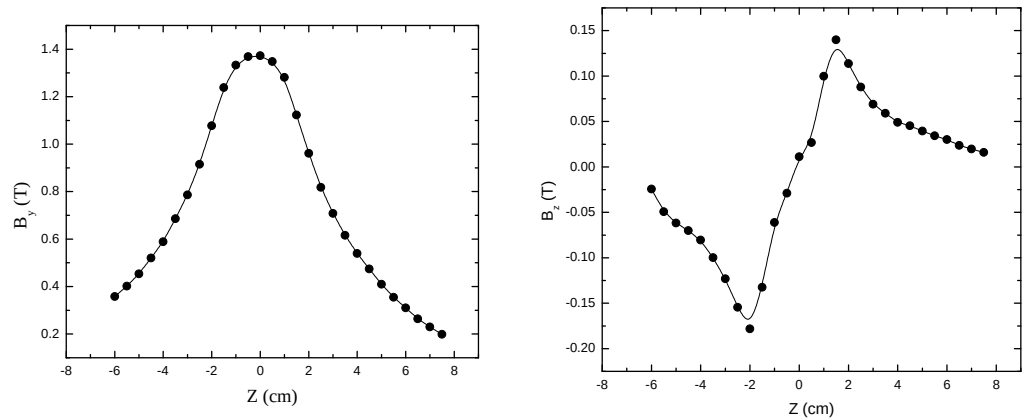


Figure 3.1: Magnetic field profiles for the 1.5 T electromagnet: (a) B_y profile, and (b) B_z profile

3. METAL DEPOSITION AND DISSOLUTION IN MAGNETIC FIELDS

3.2.2 Results and Discussion

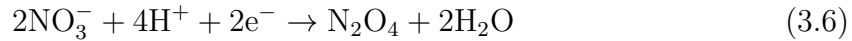
Active corrosion occurs in electrodes where there is no passive layer. At low pH the anodic dissolution of a Mn electrode in acidified KNO_3 solution,



is balanced by a cathodic reaction (oxidising agent) such as



or



The reaction 3.5 is known to be controlled by kinetics whereas reaction 3.6 may be controlled by kinetics or diffusion (mass transport). For example, the corrosion of iron is controlled by diffusion in solutions of nitric acid [18] whereas in H_2SO_4 solutions it is kinetically controlled.

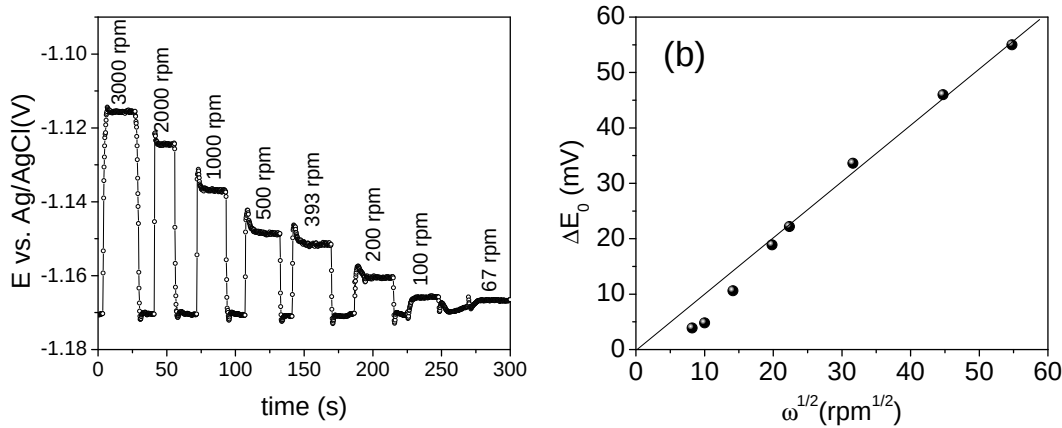


Figure 3.2: (a) Rest potential shift of Mn dependence on the rotation of an RDE electrode and (b) Levich plot of the rest potential shift. The electrolyte contains 1 M KNO_3 with pH 0.1 adjusted with HNO_3 .

Fig. 3.2a shows the variation of the rest potential with the rotation of a rotating disc electrode (RDE). After the rotation is started, the rest potential rapidly reaches a plateau. The same is observed when the rotation is stopped. A linear relationship between the rest potential shift and the square root of the rotation speed is obtained in the Levich plot shown in fig. 3.2b. This indicates that the rate-determining step associated with reaction 3.6 is diffusion. Therefore, changes in the mass-transport of cathodic reaction (eqn. 3.6) are responsible for changes in the rest potential. This idea is illustrated in fig. 3.3. The rotation enhances the transport of NO_3^- toward the electrode surface feeding the reaction 3.6 and therefore increasing the limiting current j_L . As the anodic current associated with the corrosion of the electrode increases to

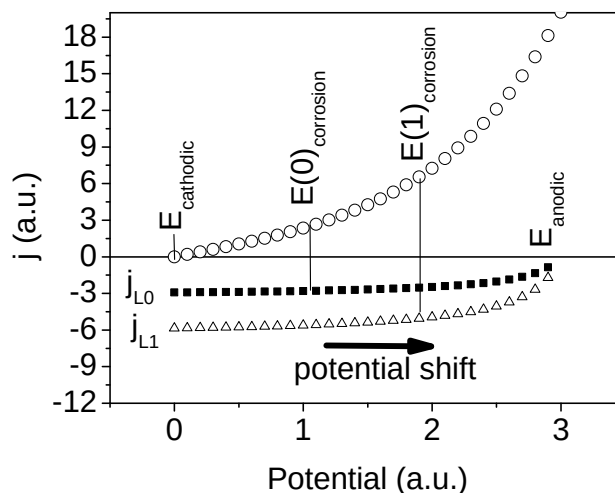


Figure 3.3: Rest potential shift induced by changes in the cathodic limiting current. E_{cathodic} , $E(0)_{\text{corrosion}}$, $E(1)_{\text{corrosion}}$, E_{anodic} stand for the standard potential of the electrode, corrosion potential associated with the cathodic limiting current (j_{L0} , j_{L1}) and the standard reduction potential of the cathodic reaction, respectively. If the cathodic limiting current is enhanced, an anodic shift [$E(1)_{\text{corrosion}} - E(0)_{\text{corrosion}}$] is observed which denoted by the arrow.

match a greater cathodic limiting current j_L , the rest potential shifts to towards more positive values (anodic potential shift).

The behaviour of the field induced rest potential shift of Mn, along with a collection of other metals, is illustrated in fig. 3.4 as the field is turned on and off. The rest potential rapidly changes with the applied magnetic field. This behaviour is similar to that seen in the rotating disc electrode experiments (Fig. 3.2a), which indicates that both the forced convection and the magnetic field acts in a similar way to change the rest potential. So the question now arises, how does the field-induced change in rest potential come about?

The answer is that the magnetic field induces convection on a microscale in the vicinity of the corroding electrode enhancing the transport of NO_3^- which feeds reaction 3.6. This is equivalent to the forced convection produced by rotating the electrode, which is depicted in fig. 3.3. However, the limiting current is now controlled by the magnetic field instead of the rotation. At zero field the rest potential is $E(0)_{\text{corrosion}}$ and the limiting current is j_{L0} . When a magnetic field is applied the limiting current is enhanced j_{L1} and thereby an anodic shift is induced, $\Delta E(B)$.

The observation of the rest potential shift for ferromagnetic, paramagnetic and diamagnetic materials (table 3.1) establish that a ferromagnetic electrode is *not* essential for the observation of the rest potential shift effect. The important feature of the system is that the electrode should be actively corroding and the corrosion should be mass transport limited.

The magnetic field must influence the corrosion through a combination of either the

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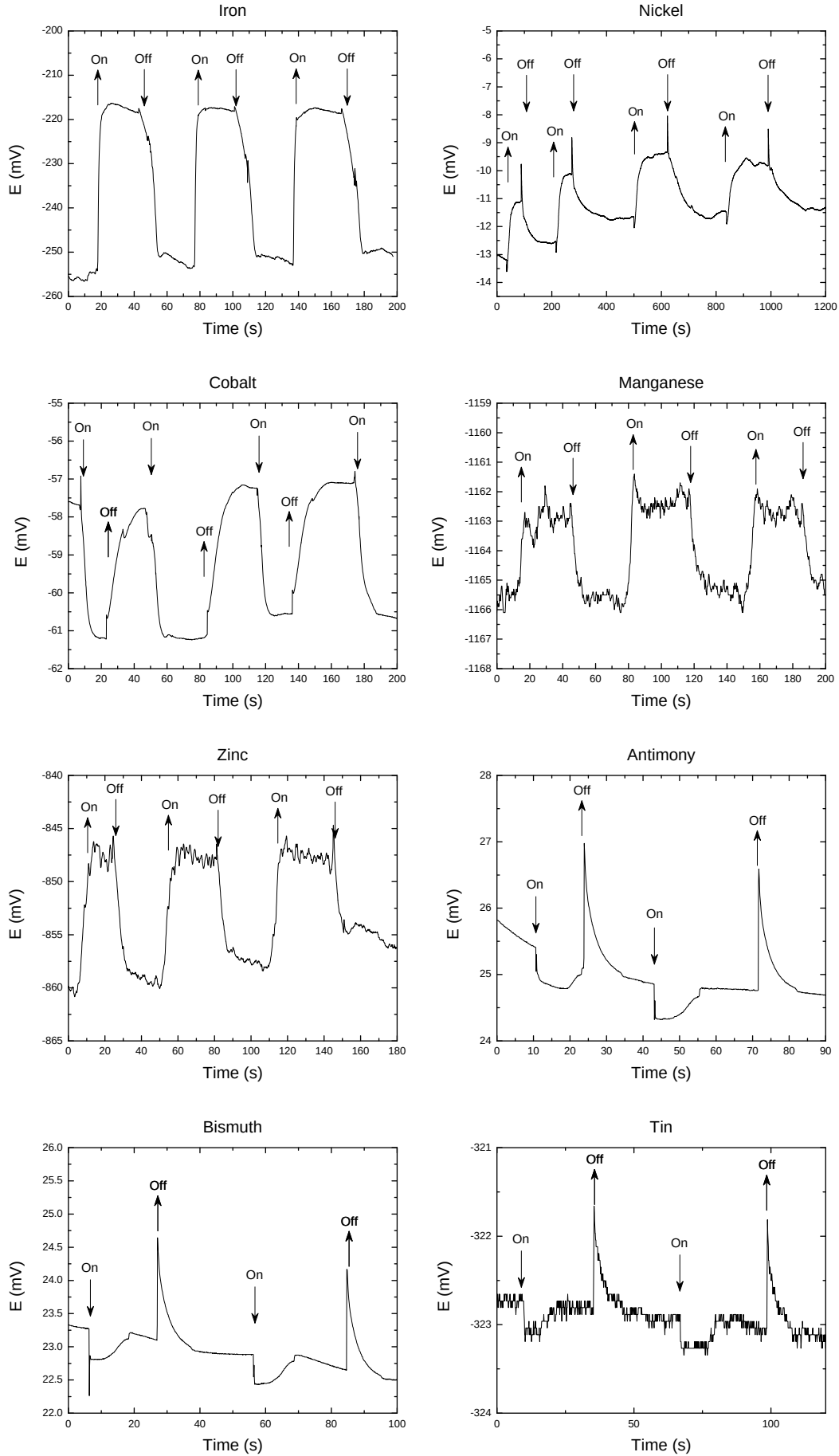


Figure 3.4: Changes in the rest potential of a number of metal electrodes in 1 M KNO_3 as a 1.5 T field is turned on and off, (a) Fe, (b) Ni, (c) Co, (d) Mn, (e) Zn, (f) Sb, (g) Bi, and (h) Sb.

magnetic field gradient, or the Lorentz force. The concentration gradient force $\mathbf{F}_{\nabla c}$ has already been discounted for numerous reasons, but even if it did exert an influence in some cells it can still safely be discounted because the reactants of reaction 3.6 are all diamagnetic and would not be attracted to the electrode, and thereby cannot explain any enhancement. Furthermore, the results for zinc in KNO_3 demonstrate that it is possible to observe a shift in a system that contains no paramagnetic ions.

The observation of the field-induced rest potential shift for non-ferromagnetic Mn, Zn, Bi, Sn and Sb also, rules out the field gradient force as a primary factor. The rest potential shift can be observed for non-magnetic electrodes provided they corrode under mass transport control. Additionally, the applied magnetic field is uniform over the cell, so there is no magnetic field gradient.

Consequently, the Lorentz force $\mathbf{F}_L$ is identified to be responsible for the field-induced rest potential. Magnetohydrodynamic flow is known to be produced by $\mathbf{F}_L$, and enhancement of the electroplating current [20, 21] in a mass transport limited regime is often observed. No *net* current flows at the rest potential and $\mathbf{J} \times \mathbf{B}$ is therefore expected to be zero on average. However the effects on the balancing cathodic and anodic currents are different, as shown in Fig. 3.3. Some sites on the electrode act as cathodes and others as anodes allowing a flux of current between them. An electronic current goes through the electrode and an ionic current flows from different anodic and cathodic sites on the electrode surface on a microscopic scale. These corrosion cells are typically $10\ \mu\text{m}$ in size [19]; and an enhancement of the flow on a small scale near the electrode surface is possible. This micro-magnetohydrodynamic flow is the principal factor behind the enhancement of the mass transport limited cathodic reaction, which in turn produces the field-induced rest potential shift.

Table 3.1: Magnetically-induced rest potential shift for several electrodes in 1 M KNO_3 pH 0.1. A 1.5 T magnetic field was applied parallel to the electrode surface. *Only exhibited a temporary rest potential shift, see fig.3.4.

Electrode	Magnetic Ordering	ΔE_0 (mV)
Fe	Ferromagnetic	36.7
Ni	Ferromagnetic	2.2
Co	Ferromagnetic	-3.5
Mn	Paramagnetic	3.0
Zn	Diamagnetic	12.1
Sb*	Diamagnetic	-0.6
Bi*	Diamagnetic	-0.5
Sn*	Diamagnetic	-0.4

The equivalence of the stirring induced by the micro-MHD effect and the RDE can be shown by calculating the flow velocity, v , for each case, when the potential shift is the

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same. For manganese, an electrode with a rotation speed of 67 rpm, and a field of 1.5 T both produce a potential shift of 4 mV. If L is the distance between the cathodic and anodic sites on the corroding electrode (10 μm), the flow velocity induced by the Lorentz force is approximately

$$v = \left(\frac{2LjB}{\rho} \right)^{1/2} \quad (3.7)$$

where j is the corrosion current density, B is the magnetic flux, and ρ is the density of the electrolyte. The corrosion current in the magnetic field was 147 mA cm^{-2} , the density of the electrolyte is 1060 kg m^{-3} , and L is 10 μm . This gives a value of $v = 6.5 \text{ mm s}^{-1}$. According to Levich, the flow velocity at the surface of an RDE is [22]

$$v = f\omega r \quad (3.8)$$

where r is the radius of the electrode (4.5 mm), ω is the angular velocity of the electrode, and $f \approx 0.2$. This gives a value of $v = 6.3 \text{ mm s}^{-1}$ at the edge of the electrode, which agrees with the value inferred from the field-induced flow. This indicates that the two systems are equivalent, and that the effect of the magnetic field is to induce flow on the 10 μm scale of the corrosion cells on the electrode surface.

While a magnetic field induced rest potential shift of Sb, Bi, or Sn can be observed, they are only transient effects. In acidified KNO_3 solution these metals passivate, and the rest potential relaxes back to the zero field value. The sudden voltage spikes after turning off the magnetic field are a result of the decay of MHD-driven convection; during which time the electrode surface reaches a new equilibrium. Finally, it can be noted that the rest potential shift measured for Co, Sb, Bi and Sn is opposite in sign (a negative shift) compared to the other metals. This is possibly due to the preponderant influence of the magnetic field on the anodic site reactions.

3.3 Copper deposition under vertical magnetic fields

An EG&G PAR 270 potentiostat was used to control and monitor the current and potential in conjunction with an electrochemical quartz crystal microbalance (EQCM). Both were controlled simultaneously using Labview, and the EQCM consisted of a Hameg HM8122 Counter Timer, Maxtech Ltd. model PL-70 resonator and a 5 MHz gold plated 1" diameter quartz crystal from Testbourne Ltd, with an active area of $5.1 \cdot 10^{-4} \text{ m}^2$. The Z-Matching Method was used for calculating the mass from the change in frequency [23], and

$$\Delta M = \frac{N_q \rho_q A}{\pi Z f_d} \tan^{-1} \left[Z \tan \left(\pi \frac{f_q - f_d}{f_q} \right) \right] \quad (3.9)$$

where ΔM is the change in Mass (g), N_q is $1.668 \cdot 10^5$ ($\text{cm}^2 \text{s}^{-1}$), ρ_q is the density of quartz = 2.648 (g cm^3), A , is the electrode area (cm^2), Z is the impedance ratio = Z_q/Z_d , f_d is the frequency of the loaded crystal (Hz), and f_q is the frequency of the unloaded crystal (Hz).

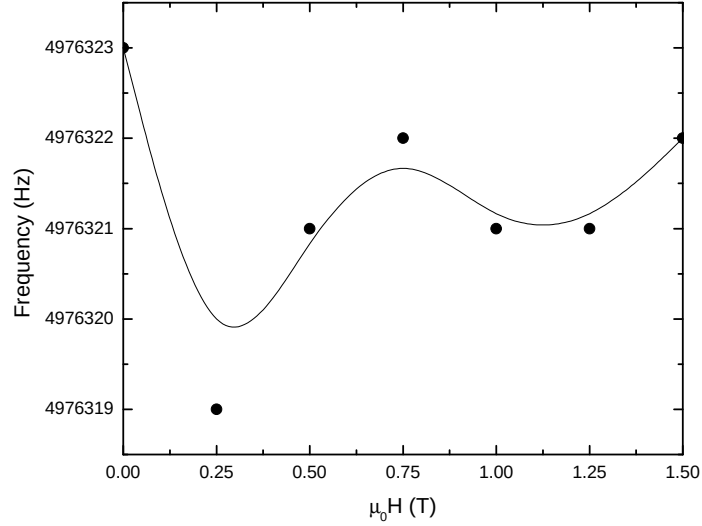


Figure 3.5: The frequency response of the quartz crystal microbalance, showing it is unaffected by large external magnetic fields.

The copper current was then calculated from the rate of change of mass dm/dt via

$$I_{\text{Cu}} = \frac{dm}{dt} \frac{nF}{m_{\text{Cu}}} \quad (3.10)$$

where $n = 2$ is the number of electrons transferred, F is Faraday's constant, and m_{Cu} is the molar mass of copper. All solutions used consisted of 0.2 M CuSO_4 and 1.2 M H_2SO_4 , experiments were carried out in a 100 ml perspex beaker containing 70 ml solution placed at the center of a cryogenic, superconducting 5.5 T magnet (see fig. 3.6), which provided vertical fields, with a uniformity of 0.10 % in a 10 mm diameter spherical volume. The quartz crystal resonator was checked to ensure that the magnetic field did not influence the measured frequency (fig. 3.5), and all potentials were measured versus a sat. KCl, Ag/AgCl reference electrode.

Potentiostatic, galvanostatic, linear sweep voltammogram experiments were carried out for a range of voltages and currents from 0 – 1.5 T, and the behaviour of the copper and hydrogen currents were studied.

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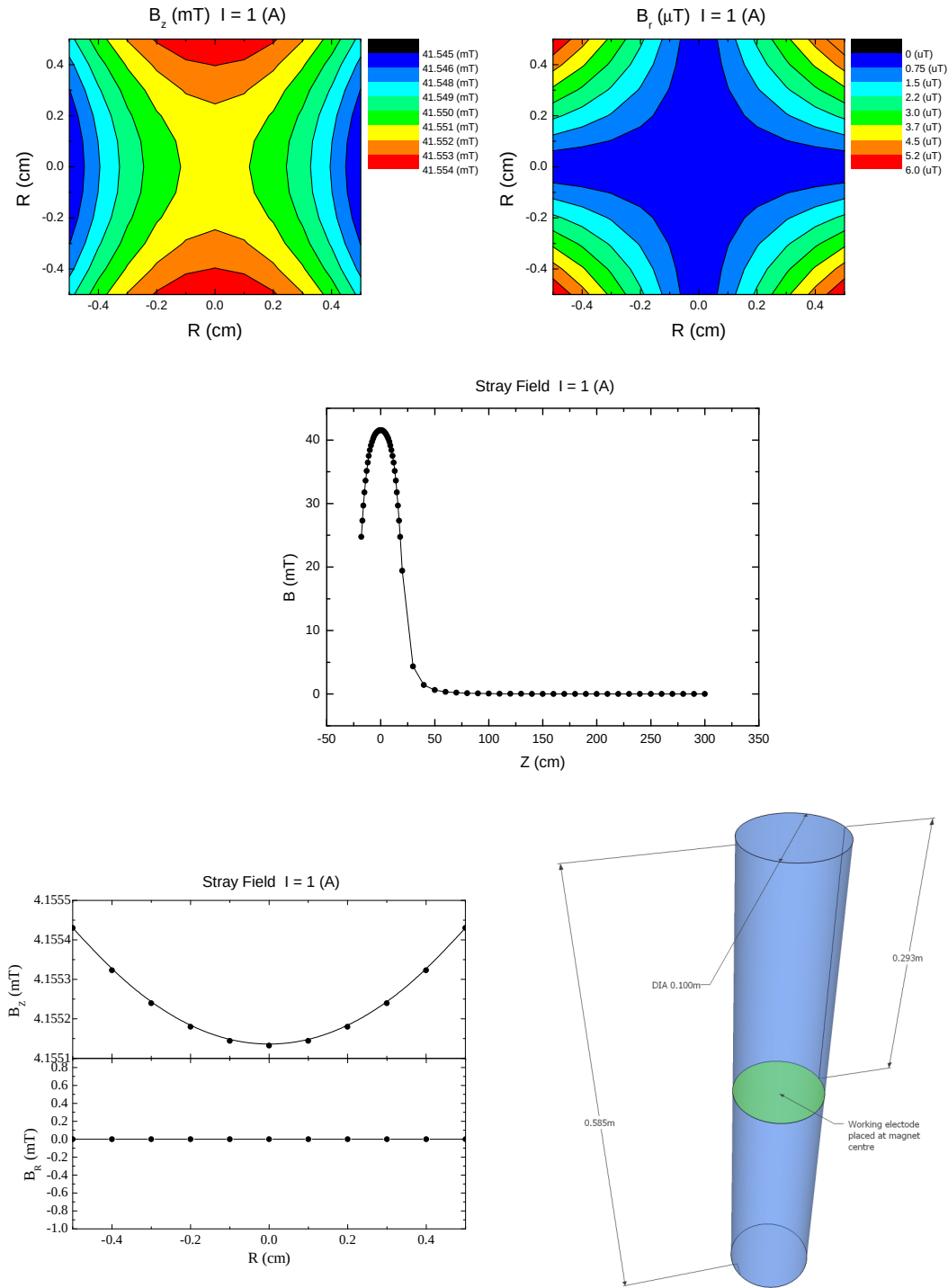


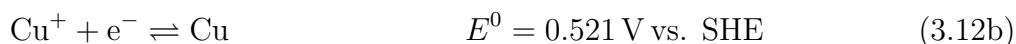
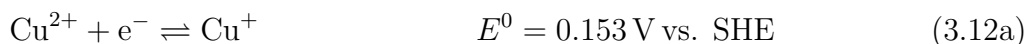
Figure 3.6: Magnetic field profiles for the 5 T magnet; the coils are energised with 1 A: (a) the axial field in the xy plane at the centre of the magnet ($z = 0$), (b) the radial field in the xy plane at the centre of the magnet ($z = 0$), (c) the axial field along the central axis ($R = 0$), (d) the axial field at the centre of the magnet ($z = 0$) in the radial direction, and (e) sample space geometry.

3.3.1 Cyclic Voltammograms

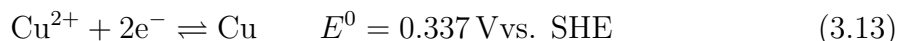
Cyclic voltammetry was performed to identify the kinetically- mass transport- and mixed-controlled regions; and their response under applied magnetic fields. Metallic copper, cupric (Cu^{2+}), and cuprous (Cu^+) ions interact with one another through



which has an equilibrium constant of $K_{eq} = [\text{Cu}^+]^2 / [\text{Cu}^{2+}] = 6.6 \cdot 10^{-7} \text{ M}$ [24]. If a Cu working electrode was used with the 0.2 M CuSO_4 bath, 0.4 mM Cu^+ would be generated at the electrode surface at the open circuit potential. However a gold plated quartz crystal was used, and Cu^+ ions are easily oxidised by dissolved oxygen in solution, so that this equilibrium is not reached in this setup. Under conditions where the reaction is shifted towards the right, i.e. the half-reaction on the right is more favourable, the reaction is referred to as comproportionation, and to the left as disproportionation. Cu deposition goes through two steps



The standard potential E^0 of the overall reaction is



which is the average of the standard potentials for (3.12a) and (3.12b). The rate-determining step is the formation of Cu^+ as under normal conditions it is more noble than Cu^{2+} .

Examining the cyclic voltammogram at zero field (black curve, fig. 3.7), in the initial negative sweep there is a peak in the current corresponding to the depletion of cupric ions at the electrode surface at more negative voltages. Beyond this voltage the $\text{Cu}^{2+} + \text{e}^- \rightleftharpoons \text{Cu}^+$ reaction rate increases, along with the hydrogen evolution reaction increases, producing more Cu^+ and H_2 and the magnitude of the current thus increases. On the return positive sweep disproportionation begins, i.e. dissolution of Cu from the surface, the Cu^+ related peak is no longer observed, and the magnitude of the current is observed to be larger. This is because the concentration of Cu^+ has already been depleted from the surface, and thus by the Nernst equation disproportion is favoured to return to equilibrium, which cannot occur since the potential is scanned continuously. Once a magnetic field is applied parallel to the electrode surface the mass transport region of the cyclic voltammogram is altered. However, first looking at the kinetically controlled region (0 V to -0.65 V) there is a small but measurable difference between the zero field sweep and the non-zero field sweeps; but there is almost no difference *between* the different applied fields. At more negative potentials the currents begin

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to diverge, with the greatest differences at the most negative potentials. As already stated reaction (3.12a) is the rate determining step in the deposition of Cu metal, so the primary effects must be on this step. This region is mass-transport limited, and indicates that the magnetic influence is convective in nature. From previous discussions §2.5, we know that the field gradient force can only influence convection, which can be discounted since the measurements were carried out in the uniform region of the magnet (see fig. 3.6). This leaves only the Lorentz force, acting on the mass-transport limited Cu^{2+} ions, which has been well studied in the past (see §2.7). The questions we now pose are, which reaction is more favoured by the magnetic field (hydrogen evolution or copper deposition), and by how much? To answer these questions, potentiostatic and galvanostatic deposition was carried out on EQCMs.

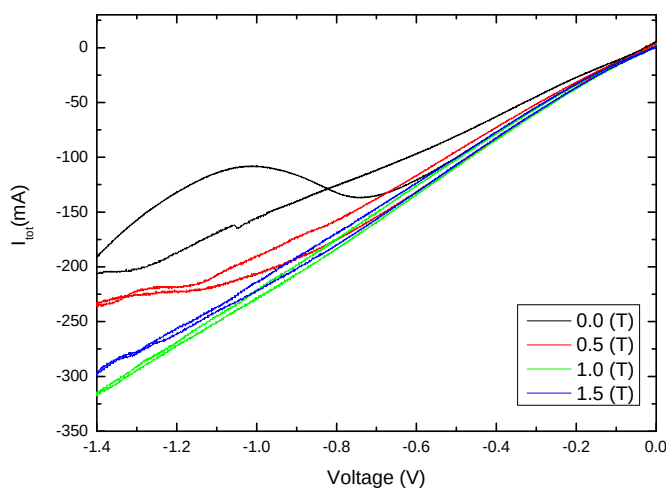


Figure 3.7: Linear sweep voltammograms for Cu deposition under a range of applied magnetic fields.

3.3.2 Potentiostatic Deposition

Cu was deposited on the Au plated EQCM at -1 V, -0.4 V and -0.2 V. At low applied potentials (-0.2 V), the hydrogen current is unaffected by any MHD stirring from the applied magnetic field. This is because at low potentials the hydrogen current is still kinetically controlled. Even at moderate to high potentials (-0.4 V, -1.0 V) the hydrogen current is only marginally influenced by the magnetic field, compared to the copper current; thus indicating that in this range the $\text{Cu}^{2+} \rightarrow \text{Cu}$ reaction is mass transport limited, unlike the hydrogen reaction, and since the field gradient is negligible, the effect comes from MHD stirring of the solution.

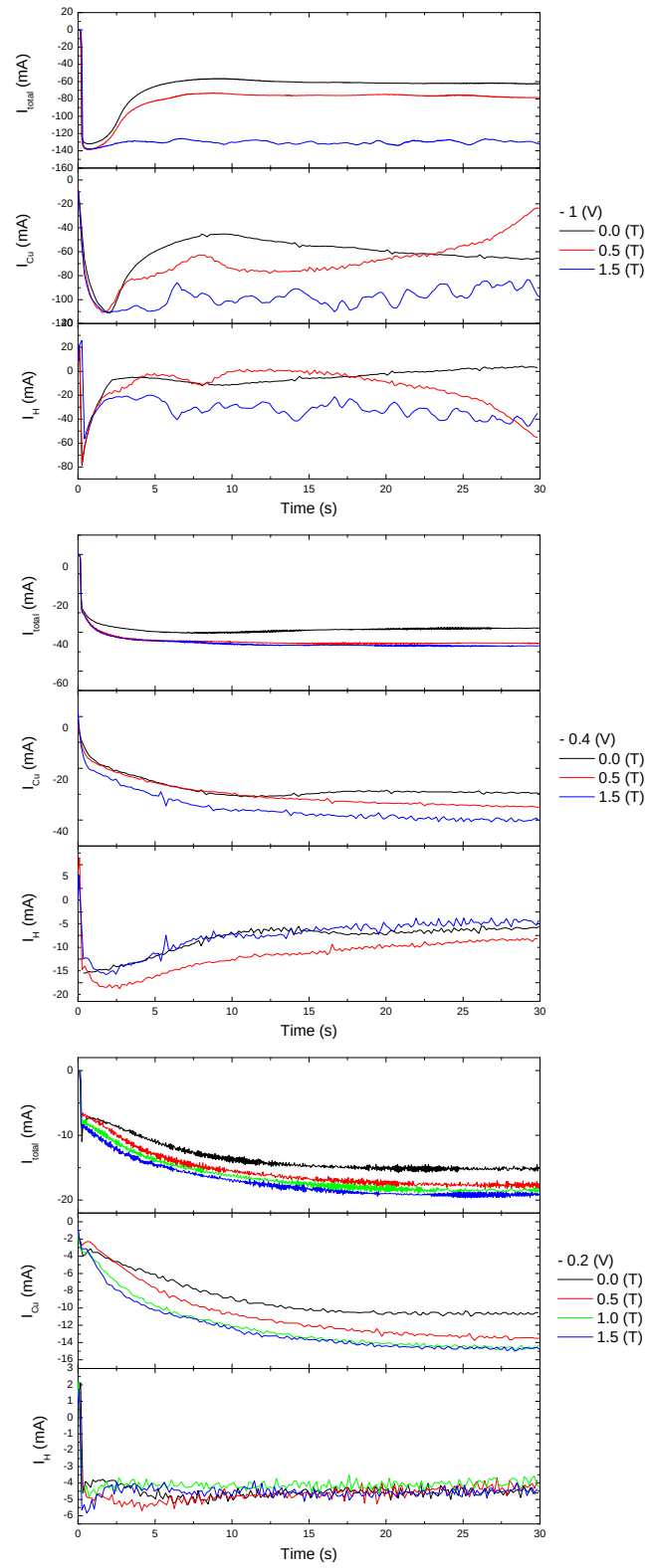


Figure 3.8: Potentiostatic deposition of Cu over a range of applied magnetic fields for (a) -1 V, (b) -0.4 V, and (c) -0.2 V.

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Table 3.2: Limiting currents for potentiostatic depostion at -0.2 V

B T	I_{tot} mA	% Change	I_{cu} mA	% Change
0	-15.14	0	-10.5	0
0.5	-17.5	16	-13.5	29
1	-18.66	23	-14.3	36
1.5	-19.2	27	-14.8	41

Table 3.3: Limiting currents for potentiostatic depostion at -0.4 V

B T	I_{tot} mA	% Change	I_{cu} mA	% Change	I_h mA	% Change
0	-37.8	0	-29.7	0	-8.1	0
1	-45.6	21	-35.1	18	-6.8	-16
1.5	-47	24	-40.2	35	-10.7	32

Table 3.4: Limiting currents for potentiostatic depostion at -1.0 V

B T	I_{tot} mA	% Change	I_{cu} mA	% Change	I_h mA
0	-61	0.00	-65.7	0	3
0.5	-75.8	24	-23.7	-64	-55.2
1	-90.9	49	-20.6	-69	-70.4
1.5	-129.2	112	-97.9	49	-35.3

3.3.3 Galvanostatic Deposition

Changing to galvanostatic deposition, a similar situation occurs. First, examining the voltage response at zero field for a range of currents (fig. 3.9), it is immediately noticeable that there are three different types of responses.

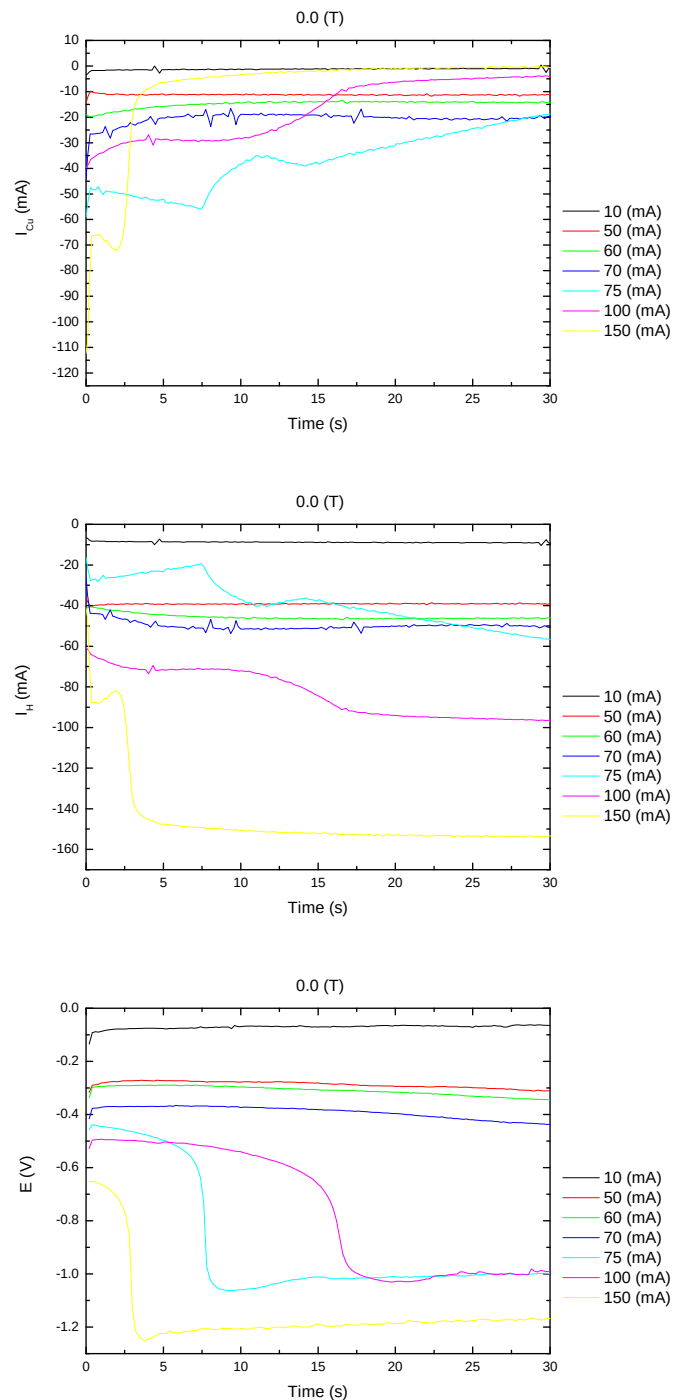


Figure 3.9: Galvanostatic deposition of Cu at various currents, under zero field. (a) Copper current, (b) HER current, and (c) voltage response.

At very low currents (10 mA), the potential remains at close to -0.1 V, indicating that the deposition is purely kinetically controlled. Then there is an intermediate regime,

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from 50 mA to 75 mA under which there is some mixed control; and finally at larger currents (> 75 mA) Cu^{2+} ions are rapidly removed from solution near the electrode, creating a mass transport limited system, and the voltage ramps towards more negative voltages to maintain the current by switching to hydrogen production.

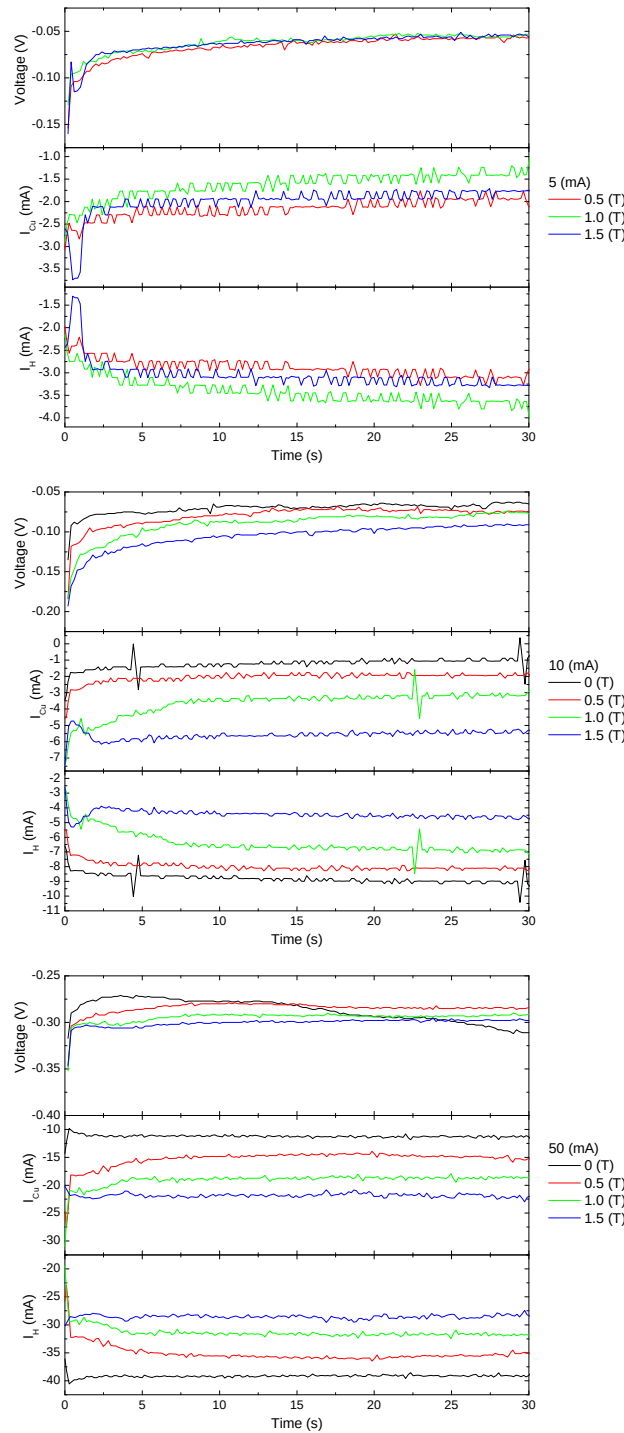


Figure 3.10: Galvanostatic deposition of Cu at various currents, and zero field, (a) 5 mA, (b) 10 mA, and (c) 50 mA.

The magnetic field has little or no effect on the smallest currents (5 mA), at -0.1 V both the hydrogen and copper currents are far from their standard potentials, and

are kinetically controlled. However, beginning with the 10 mA deposits, it is clear that the hydrogen reaction is suppressed while the copper current is favoured, and this continues for all galvanostatic measurements up to 150 mA. As previously noted at zero field, for current magnitudes greater than 75 mA the driving potential rapidly decreases towards hydrogen evolution to maintain the set current, as Cu^{2+} is rapidly depleted from the electrode surface. Once a field is applied, a relatively steady flux of Cu^{2+} ions are transported to the surface, the voltage remains less negative; and the magnetic field continues to suppress the hydrogen current for larger fields. The MHD effect also begins to saturate for large $I \cdot B$ products, as can be seen in figure 3.11 for the 150 mA curves. In all measurable galvanostatic cases, the Lorentz force stirring favoured the copper reaction over the hydrogen one, as the hydrogen current remained kinetically controlled.

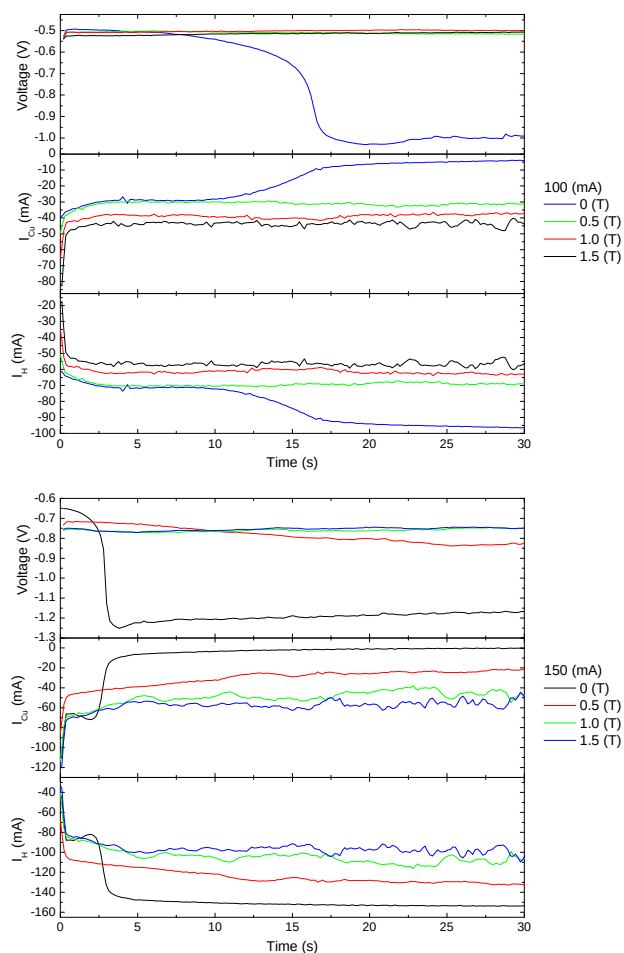


Figure 3.11: Galvanostatic deposition of Cu at various currents, and zero field, (a) 100 mA, and (b) 150 mA.

The results obtained galvanostatically are in good agreement with the responses observed by Nicolich *et al.* [25] who reported reductions in the effective overpotential when vigorous bubbling established a hydrodynamic regime in copper-hydrogen co-reduction from acid sulphate solutions. These observations also agree with the previously men-

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Table 3.5: Limiting currents for galvanostatic depostion at -5 mA

B (T)	I_{cu} (mA)	I_h (mA)
0.5	-1.9	-3.1
1	-1.4	-3.6
1.5	-1.7	-3.3

Table 3.6: Limiting currents for galvanostatic depostion at -10 mA

B (T)	I_{cu} (mA)	I_h (mA)
0	-1.1	-8.9
0.5	-1.9	-8.1
1	-3.2	-6.8
1.5	-5.3	-4.7

Table 3.7: Limiting currents for galvanostatic depostion at -50 mA

B (T)	I_{cu} (mA)	I_h (mA)
0	-1.1	-48.9
0.5	-1.9	-48.1
1	-3.2	-46.8
1.5	-5.5	-44.5

Table 3.8: Limiting currents for galvanostatic depostion at -100 mA

B (T)	I_{cu} (mA)	% Change	I_h (mA)	% Change
0	-3.9	0.00	-96.1	0.00
0.5	-31.4	705.13	-68.6	-28.62
1	-37	848.72	-63	-34.44
1.5	-42.8	997.44	-57.2	-40.48

Table 3.9: Limiting currents for galvanostatic depostion at -150 mA

B (T)	I_{cu} (mA)	% Change	I_h (mA)	% Change
0	-0.7	0.00	-149.3	0.00
0.5	-21.7	3000.00	-128.3	-14.07
1	-48.4	6814.29	-101.6	-31.95
1.5	-52.3	7371.43	-97.7	-34.56

tioned work by Diao *et al.* on hydrogen evolution in acidic solutions; who measured a reduction in the hydrogen overpotential as a function of increased magnetic field [16]. Finally, the correlations between the measured hydrogen current using the EQCM, and

potential switching in the galvanostatic curves, allow us to study the onset of hydrogen evolution solely from galvanostatic curves when it is not possible to use an EQCM. This methodology will be used in the next chapter.

3.4 Conclusion

Mass-transported limited corrosion is a necessary condition for the observation of the field-induced rest potential shift, which does not depend in an essential way on the magnetic nature of the electrode. It is a coincidence that ferromagnetic electrodes corrode in such conditions. The field-induced shift can be taken as a signature of mass transport limitation in corroding systems.

The mechanism associated with the field-induced rest potential shift is the magnetohydrodynamic stirring provided by the Lorentz force. Ionic current flows between anodic and cathodic sites in local electrochemical cells where the cathodic reaction is enhanced by magnetically-stirred solution; which is the origin of the field-induced anodic rest potential shift.

Likewise, the dominant magnetic force effect in Cu electrodeposition, in a vertical field with the cathode surface parallel to the field, is the Lorentz force which induces magnetoconvection at the electrode surface. For negative overpotentials smaller than the hydrogen reduction potential, the HER remains kinetically controlled, and all current enhancement is due to the increased flux of Cu^{2+} ions supplying the mass-transport limited copper reduction reaction.

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Chapter 4

Electrodeposition above Permanent Magnet Arrays

4.1 Introduction

In the previous chapter, we demonstrated systems where the Lorentz force $\mathbf{F}_L = \mathbf{j} \times \mathbf{B}$ is the dominant driving force in metal deposition and dissolution. Lorentz-force driven magnetoconvection on the scale of the electrochemical cell influences the width of the diffusion layer, and tends to increase the deposition rate in the mass transport limited regime in a manner equivalent to gentle stirring. These effects have been studied in detail for deposition of a number of metals including copper [1, 2], silver [3], and nickel [4] (see §2.7). The theory has been worked out in detail [5, 6], and numerical simulations seem to agree well with both the theory and the experiments [7, 8]. The magnitude of $\mathbf{F}_L$ is 10^3 N m^{-3} for $j = 10^3 \text{ A m}^{-2}$ and $B = 1 \text{ T}$, which are typical values used in the experiments below. The Lorentz force is similar in magnitude to the gravitational force density $\mathbf{F}_g = \Delta\rho\mathbf{g}$ driving convection.

Recently, there has been growing interest in the influence of magnetic field gradients on electrochemical reactions [9–14]. The relevant force density is thus $\mathbf{F}_{\nabla B} = \frac{1}{2\mu_0}\chi_m B^2 \nabla c$, which is proportional to the product of the magnitude of the field $\mathbf{B}$ and the field gradient ∇B . These quantities are proportional when the field is produced by a single magnet, but they can be controlled separately if there are different sources for $\mathbf{B}$ and ∇B . For an electrolyte with susceptibility 10^{-4} , in a field of 1 T and a field gradient of 100 T m^{-1} , the force density is $4 \cdot 10^4 \text{ N m}^{-3}$. This is more than an order of magnitude greater than the force densities introduced in the first paragraph, so the field gradient force may be expected to exert an important influence on the electrodeposit when it is present.

It should not be imagined that a magnetic field gradient can pull ions in from the solution to the vicinity of the magnet. This is impossible, because the energy of a single Co^{2+} ion with $S = 3/2$ at room temperature in a field of 1 T is $E = \mu_0 g^2 \mu_B S(S + 1) B^2 / 2k_B T = 7 \cdot 10^{-7} \text{ eV}$, which is considerably less than the thermal energy driving

4. ELECTRODEPOSITION ABOVE PERMANENT MAGNET ARRAYS

diffusion ($k_B T \sim 1/40$ eV). Likewise, the field gradient force is conservative, meaning it cannot *induce* convection, rather it can modify, or bifurcate existing convective flows. Here we set out to investigate electrodeposition in the presence of structured magnetic field patterns created by small permanent magnets, attempt to observe any modifications of the electrodeposition process, and identify the important magnetic interactions such as the field gradient force, or the magnetostatic energy.

4.2 Experimental Methods

Electrochemical measurements were carried out with an EG&G PAR 270 potentiostat. The working electrodes consisted of 50 μm thick foils of 99.9% pure silver, with an exposed circular area of 2.85 cm^2 ; a Pt mesh was used as the counter electrode, and a saturated KCl Ag/AgCl reference electrode was used to which all potentials are quoted.

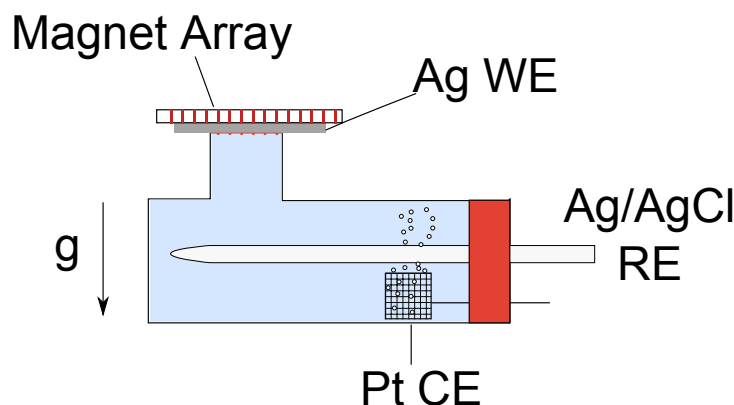


Figure 4.1: Cell geometry; the working electrode was always inverted to minimise natural convection

The baths used can be categorised under two headings, dot array baths, and anti-dot array baths. Dot array baths consisted of:

Bulk paramagnetic solutions ($\chi > 0$): 2 M CoSO_4 + 0.6 M H_3BO_3 , and 1 M CuSO_4 + 1.2 M H_2SO_4 + 0.25 mM KCl

Bulk zero susceptibility solutions ($\chi \approx 0$): 0.545 M CuSO_4 + 0.25 mM NaCl + 1.2 M H_2SO_4

Bulk diamagnetic solutions ($\chi < 0$): 0.1 M CuSO_4 + 1 M NaSO_4 + 0.1 M acetic acid + 0.1 M sodium acetate

These solutions were chosen to differentiate between bulk solution effects and interfacial effects. Two anti-dot solutions were used, the first, a highly paramagnetic solution

consisted of 1 M $\text{Dy}(\text{NO}_3)_3$ + 0.1 M CuSO_4 + 0.3 M H_3BO_3 , and the second contained dysprosium and copper salts with the same volume susceptibility: 3.3 mM $\text{Dy}(\text{NO}_3)_3$ + 0.1 M CuSO_4 + 0.3 M H_3BO_3 . All cobalt arrays were deposited potentiostatically at -1.2 V for 10 minutes. Bulk paramagnetic Cu solutions were deposited potentiostatically at -0.4 V for 20 minutes, bulk diamagnetic Cu solutions at -0.85 V for 10 minutes; and zero susceptibility Cu solutions were deposited galvanostatically for a range of currents (-5 mA to -20 mA) for 10 minutes. Both anti-dot solutions were deposited galvanostatically at -10 mA for 10 minutes.

The magnet arrays were produced from small cylindrical Nd-Fe-B permanent magnets, with a diameter of 2 mm and a height of 2 mm. The magnets were backed with soft iron sheets to concentrate the flux towards the upper side, and to give extra stability to unstable configurations, and were covered with $150\mu\text{m}$ thick parafilm to protect their surfaces from the solution, and to ensure electrodeposition occurred only on the working electrodes. $50\mu\text{m}$ thick silver foil working electrodes were placed on the parafilm directly above the magnet arrays, and the entire cell was inverted to minimise the effects of natural convection (see fig. 4.1).

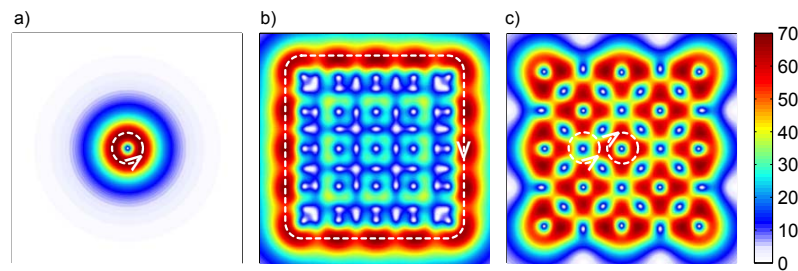


Figure 4.2: Lorentz force induced flow for (a) a single cylindrical permanent magnet, (b) a square array of magnets all magnetised in the same direction, and (c) a square array with the magnets alternately $\pm B$ in both x and y . The colour scale shows the velocity in arbitrary units, and the white arrows indicate the potential flow.

4.3 Magnetic Field Calculations

Magnetic field calculations were carried out using the surface charge model (see §2.1 and the appendices); where the magnet arrays were assumed to be composed of uniformly magnetised segments of hard, magnetically transparent, permanent magnetic material. Since the magnetisation is fixed and uniform within each segment the calculation reduces to finding the field due to a scalar magnetic charge density on each surface of every segment. The surface of each segment can be broken into simplexes, which in 3-D are right-angled triangles, and the field, H , at a point $P(x, y, z)$ is summed over the field due to each simplex. A software package developed by J. Hilton as part of his PhD thesis, Manifest, was used to calculate the field above the permanent magnet arrays used in experiments. The magnetic field and magnetic field gradient contour plots were originally written in Matlab by Lorenzo Mazza during his research in Trinity

4. ELECTRODEPOSITION ABOVE PERMANENT MAGNET ARRAYS

College Dublin. Below are the calculated magnetic fields and field gradients for the magnet arrays used:

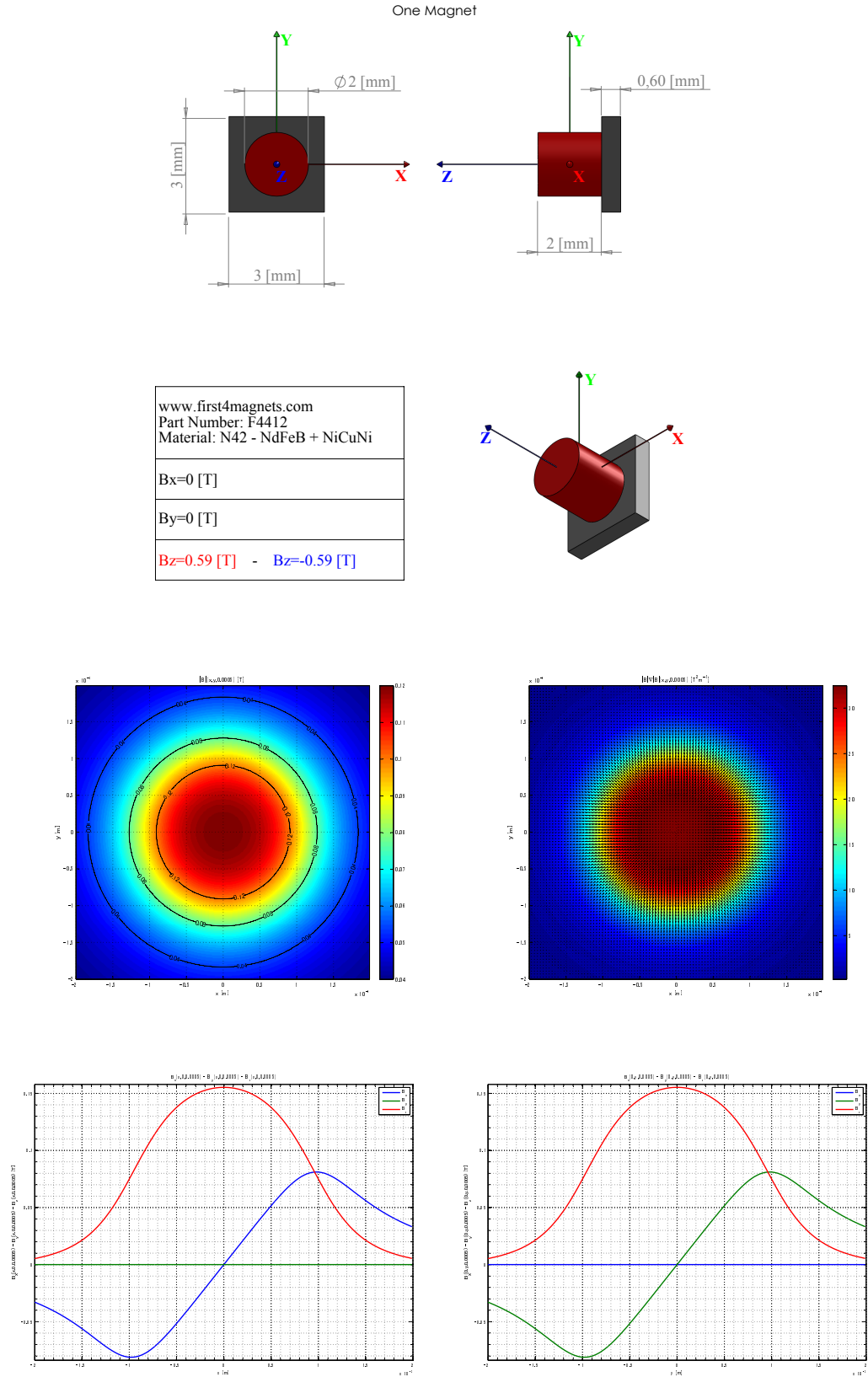


Figure 4.3: One magnet: (a) Layout, (b) $|B|$ at $z = 0.5$ mm, (c) $B \cdot \nabla B$ at $z = 0.5$ mm, (d) B_x , B_y , and B_z at $y = 0$ mm, $z = 0.5$ mm along x , and (e) B_x , B_y , and B_z at $x = 0$ mm, $z = 0.5$ mm along y

4. ELECTRODEPOSITION ABOVE PERMANENT MAGNET ARRAYS

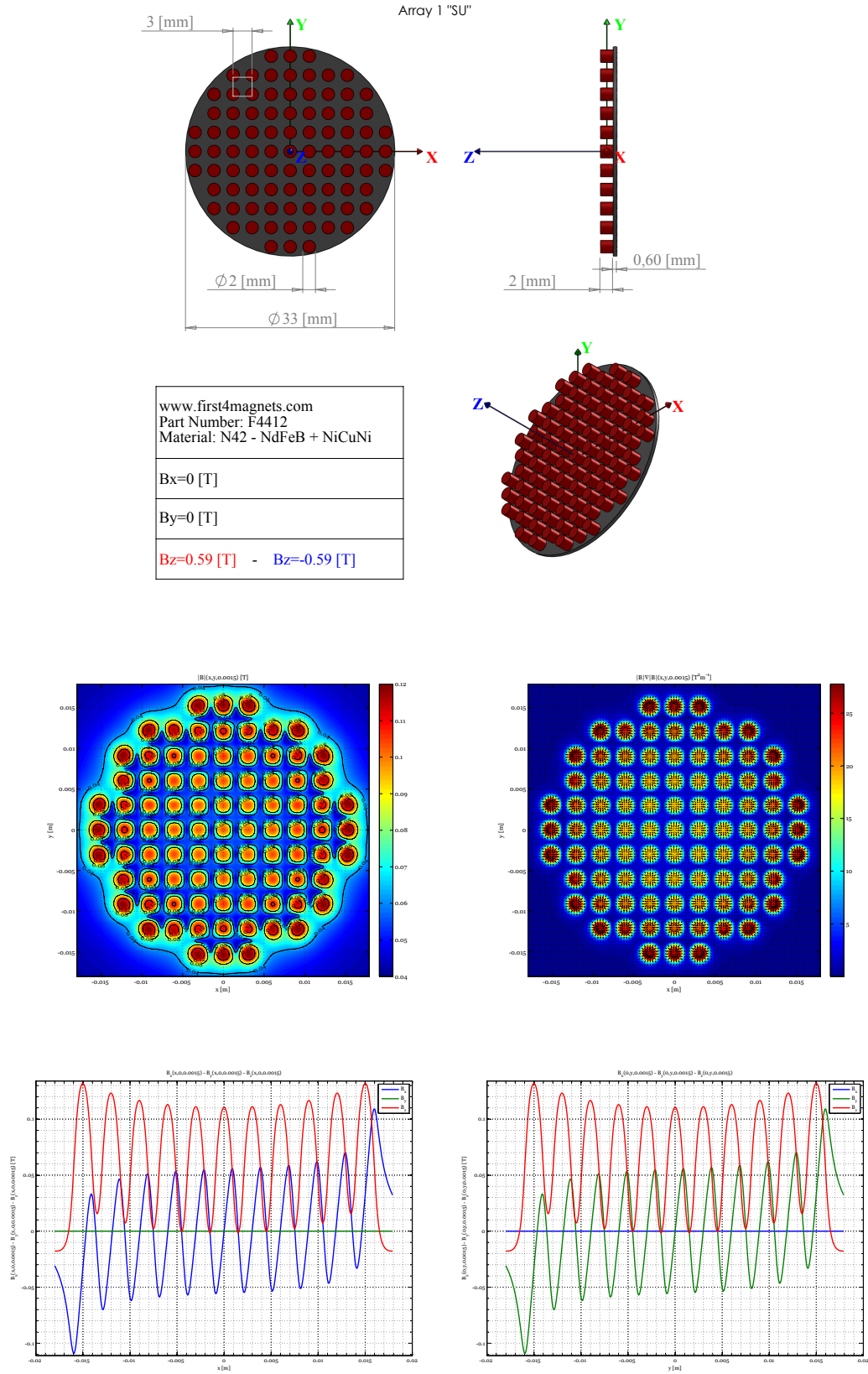


Figure 4.4: Array 1, 'SU', square lattice, all pointing 'up': (a) Layout, (b) $|B|$ at $z = 0.5$ mm, (c) $B \nabla B$ at $z = 0.5$ mm, (d) B_x , B_y , and B_z at $y = 0$ mm, $z = 0.5$ mm along x , and (e) B_x , B_y , and B_z at $x = 0$ mm, $z = 0.5$ mm along y

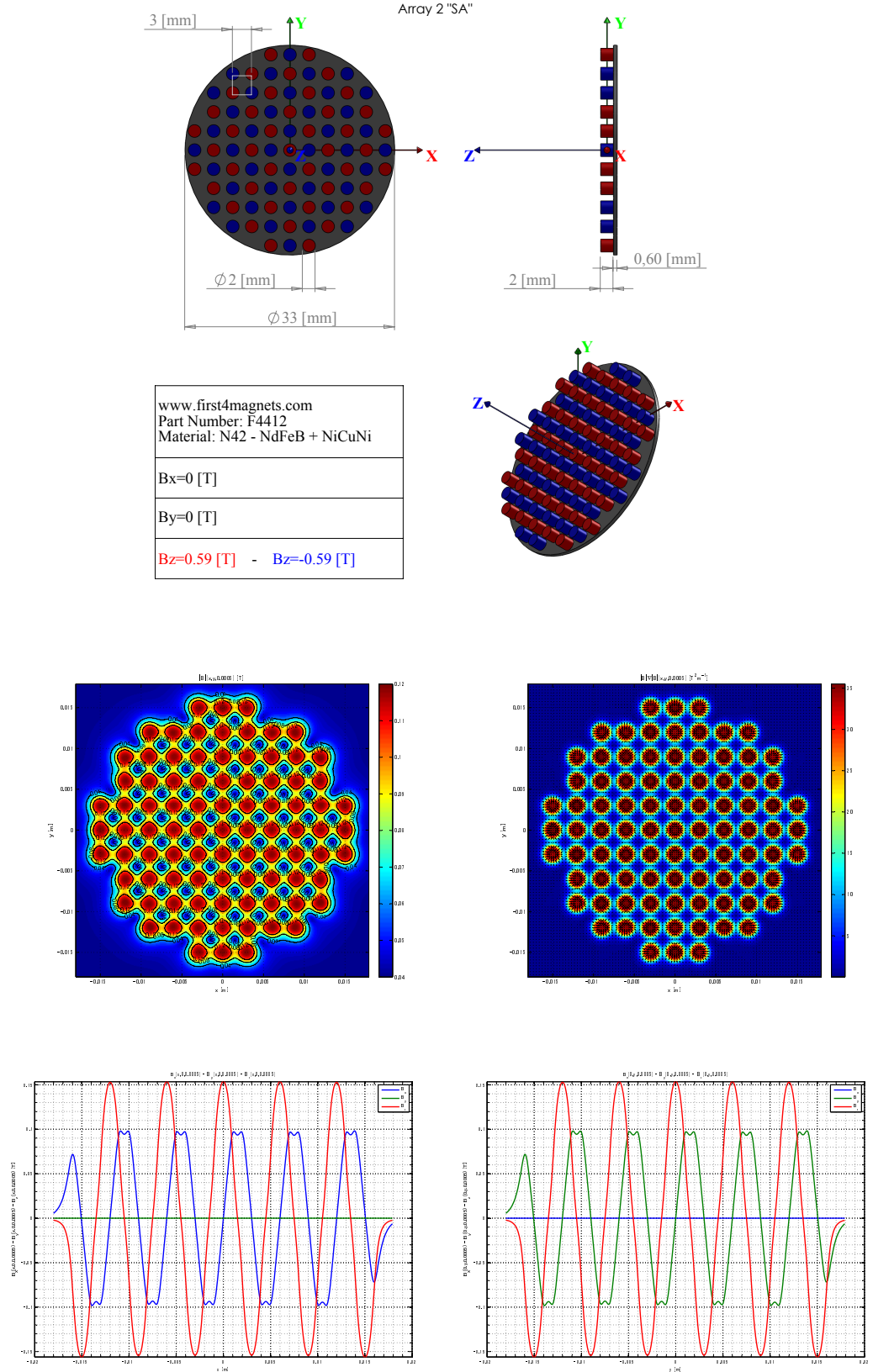


Figure 4.5: Array 2, 'SA', square lattice, alternating: (a) Layout, (b) $|B|$ at $z = 0.5$ mm, (c) $B \nabla B$ at $z = 0.5$ mm, (d) B_x , B_y , and B_z at $y = 0$ mm, $z = 0.5$ mm along x , and (e) B_x , B_y , and B_z at $x = 0$ mm, $z = 0.5$ mm along y

4. ELECTRODEPOSITION ABOVE PERMANENT MAGNET ARRAYS

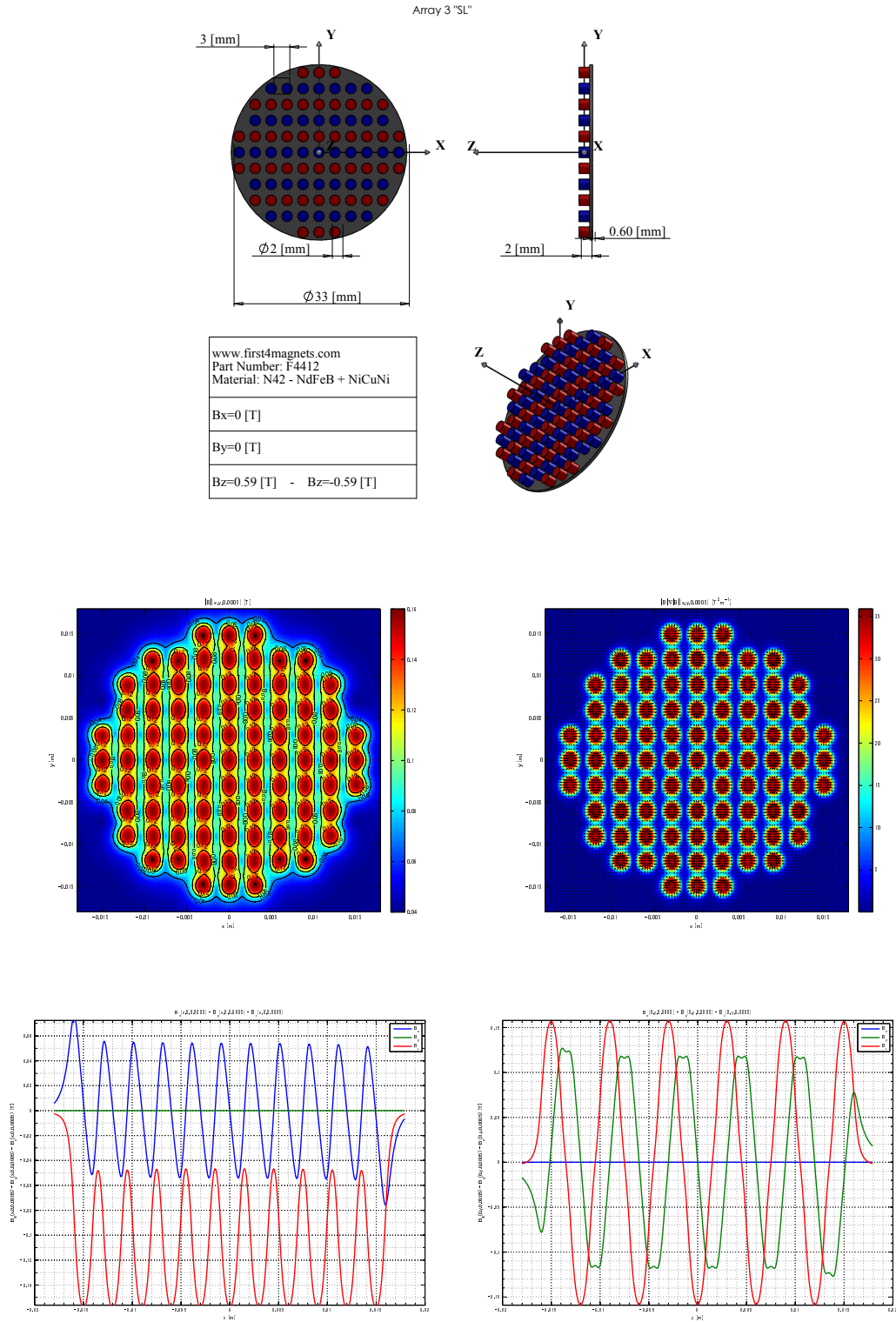


Figure 4.6: Array 3, 'SL', square lattice, line-alternating: (a) Layout, (b) $|B|$ at $z = 0.5$ mm, (c) $B \nabla B$ at $z = 0.5$ mm, (d) B_x , B_y , and B_z at $y = 0$ mm, $z = 0.5$ mm along x , and (e) B_x , B_y , and B_z at $x = 0$ mm, $z = 0.5$ mm along y

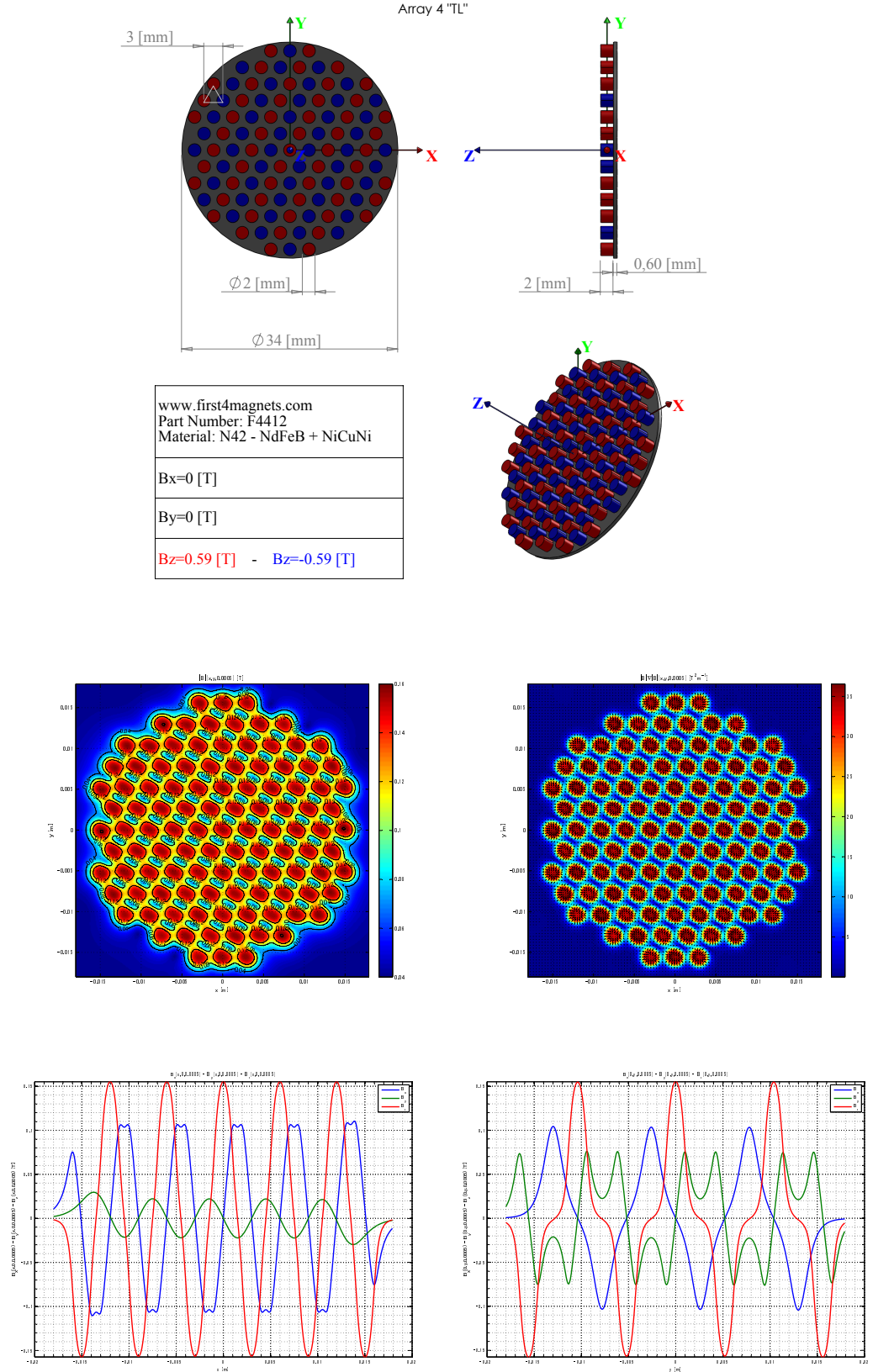


Figure 4.7: Array 4, ‘TL’, triangular lattice, line-alternating: (a) Layout, (b) $|B|$ at $z = 0.5$ mm, (c) $B \nabla B$ at $z = 0.5$ mm, (d) B_x , B_y , and B_z at $y = 0$ mm, $z = 0.5$ mm along x , and (e) B_x , B_y , and B_z at $x = 0$ mm, $z = 0.5$ mm along y

4. ELECTRODEPOSITION ABOVE PERMANENT MAGNET ARRAYS

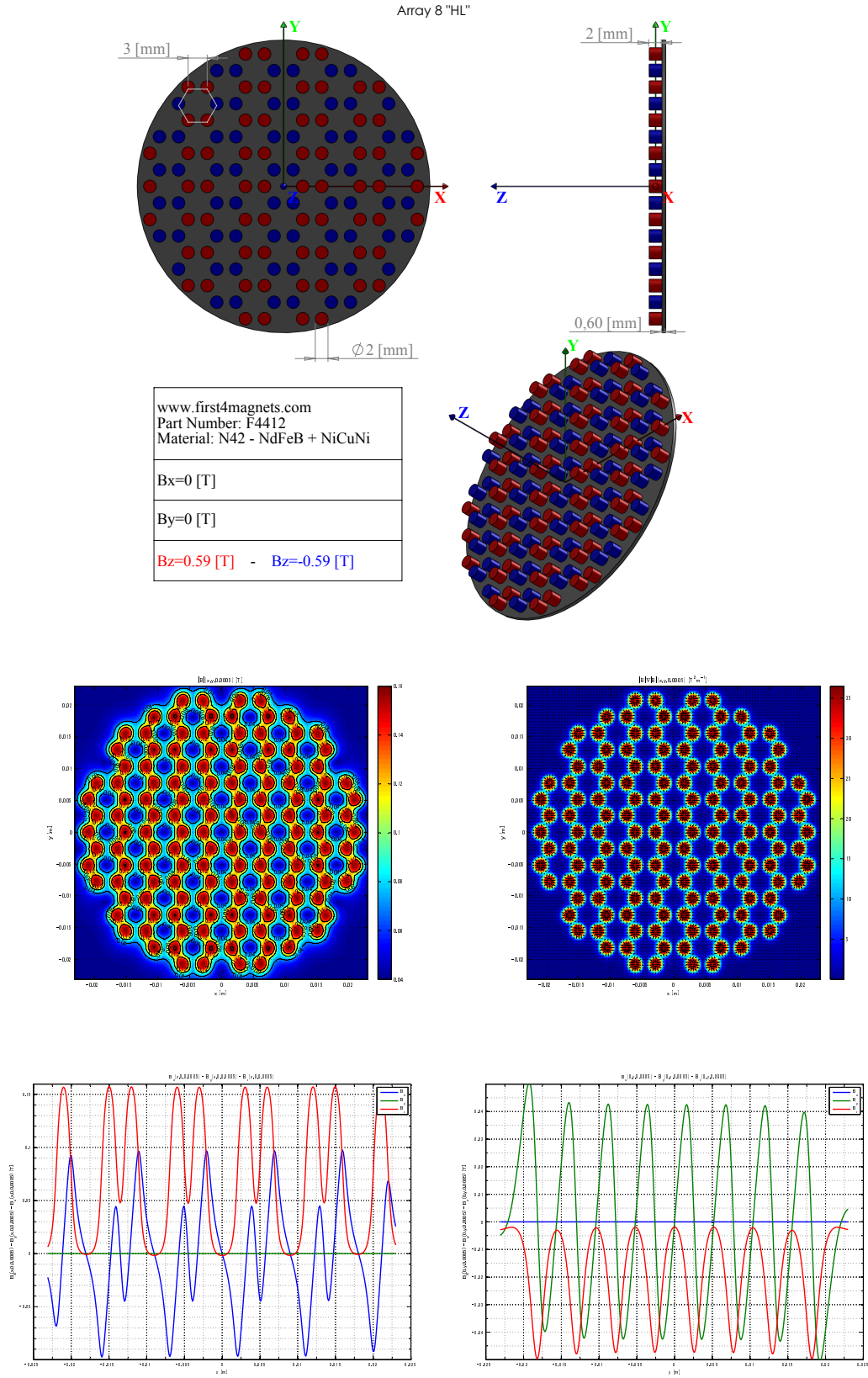


Figure 4.8: Array 5, 'HL', hexagonal lattice, line-alternating: (a) Layout, (b) $|B|$ at $z = 0.5$ mm, (c) $B \cdot \nabla B$ at $z = 0.5$ mm, (d) B_x , B_y , and B_z at $y = 0$ mm, $z = 0.5$ mm along x , and (e) B_x , B_y , and B_z at $x = 0$ mm, $z = 0.5$ mm along y

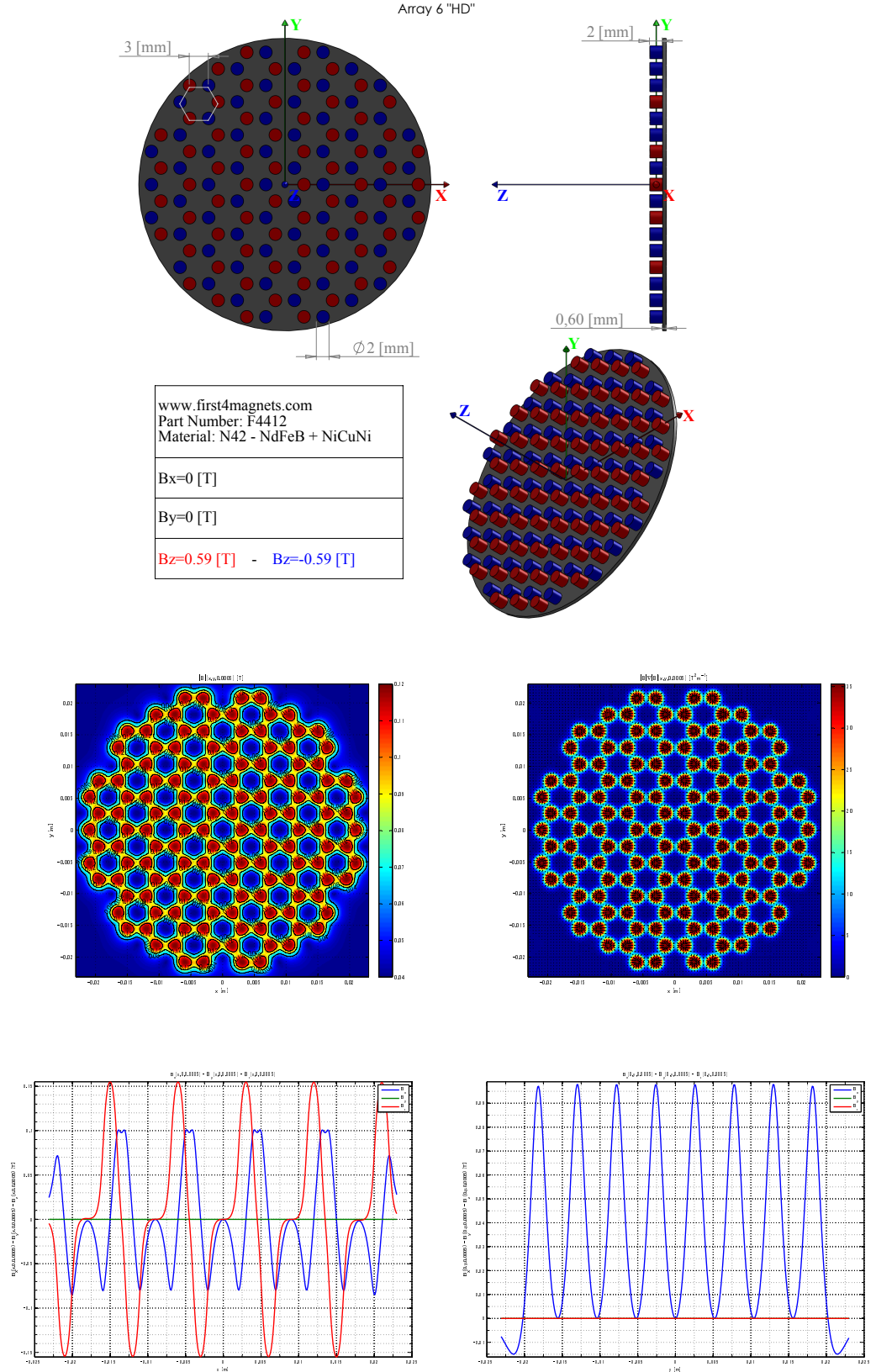


Figure 4.9: Array 6, 'HD', hexagonal lattice, diagonal line alternating: (a) Layout, (b) $|B|$ at $z = 0.5$ mm, (c) $B \nabla B$ at $z = 0.5$ mm, (d) B_x , B_y , and B_z at $y = 0$ mm, $z = 0.5$ mm along x , and (e) B_x , B_y , and B_z at $x = 0$ mm, $z = 0.5$ mm along y

4. ELECTRODEPOSITION ABOVE PERMANENT MAGNET ARRAYS

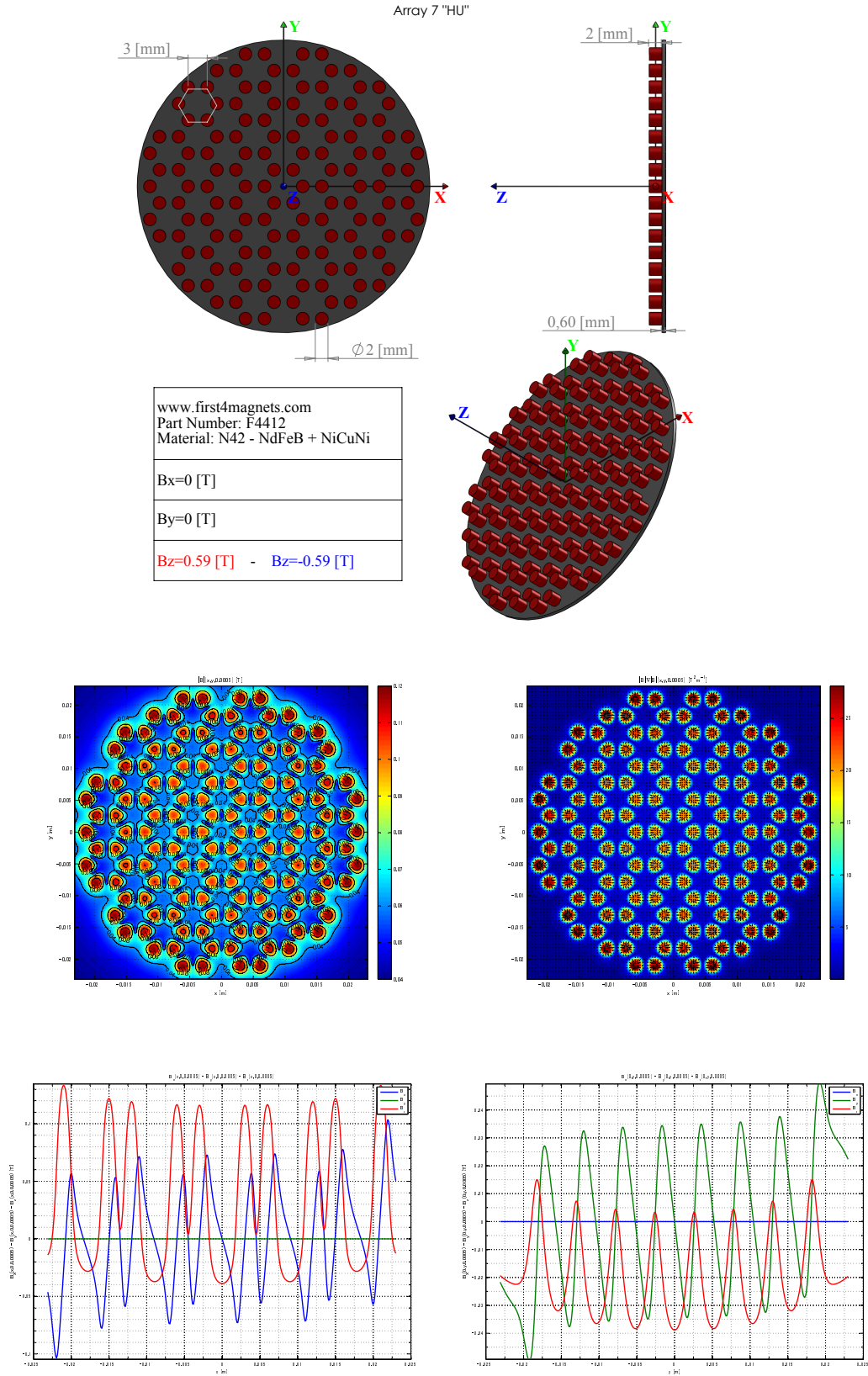


Figure 4.10: Array 7, 'HU', hexagonal lattice, all 'up': (a) Layout, (b) $|B|$ at $z = 0.5$ mm, (c) $B \nabla B$ at $z = 0.5$ mm, (d) B_x , B_y , and B_z at $y = 0$ mm, $z = 0.5$ mm along x , and (e) B_x , B_y , and B_z at $x = 0$ mm, $z = 0.5$ mm along y

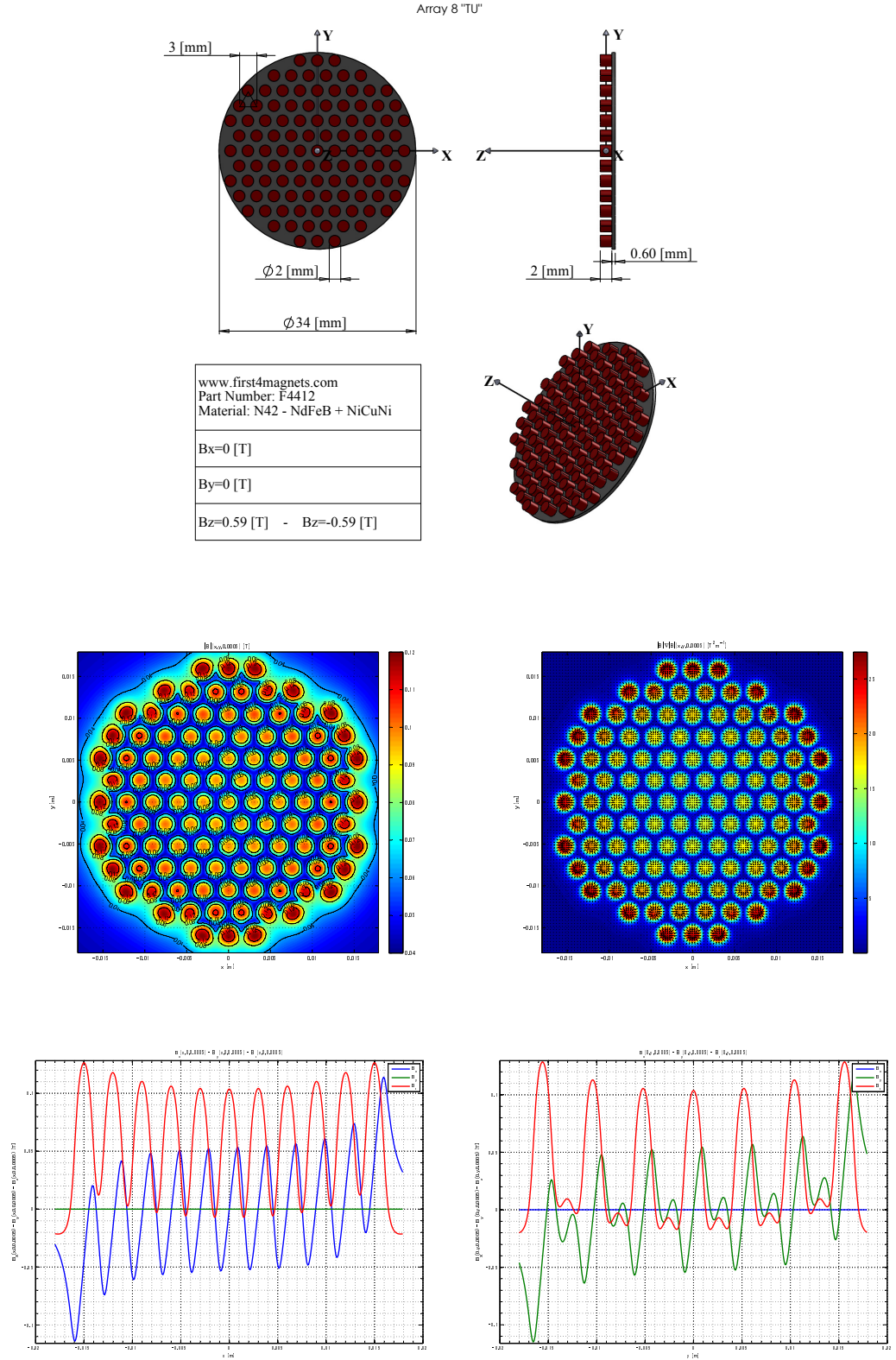


Figure 4.11: Array 8, 'TU', trigonal lattice, all 'up': (a) Layout, (b) $|B|$ at $z = 0.5$ mm, (c) $B \nabla B$ at $z = 0.5$ mm, (d) B_x , B_y , and B_z at $y = 0$ mm, $z = 0.5$ mm along x , and (e) B_x , B_y , and B_z at $x = 0$ mm, $z = 0.5$ mm along y

4. ELECTRODEPOSITION ABOVE PERMANENT MAGNET ARRAYS

4.3.1 Z dependence of field profile

The magnetic flux density decays rapidly with increasing distances from the source of the magnetic field. Examining 4.12.c –the magnetic field along the central axis of one cylindrical magnet– it is clear that the magnetic field decays rapidly with increasing distance in a fashion expected from Biot-Savart’s law (z^{-3} dependence). This has a detrimental effect on the magnetic field and field gradient contours in x - y planes with increasing z , as can be seen in figures 4.13 and 4.12. Essentially the profiles smear or broaden out as the magnitude of the field decreases while the lateral dimensions remain unchanged. This poses an extra requirement on electrode and cell design as the active cathode area must be put as close to the magnet arrays as possible. In practise this means thinner substrates, which is the rationale for choosing 50 μ m thick silver foil.

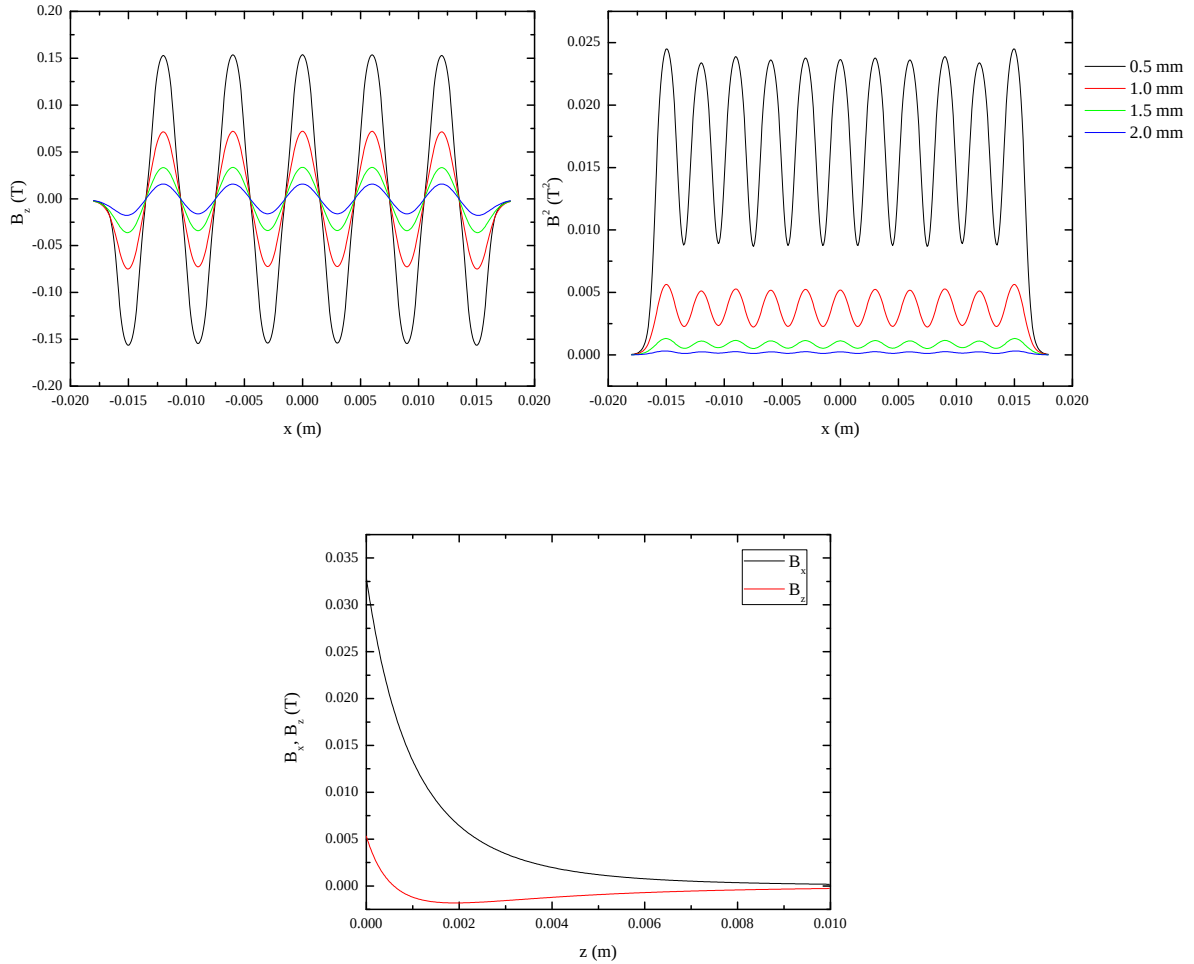


Figure 4.12: Variation of (a) B and (b) B^2 with z for a square alternating array along x , and (c) decay of B_x , B_z along the central axis of a cylinder.

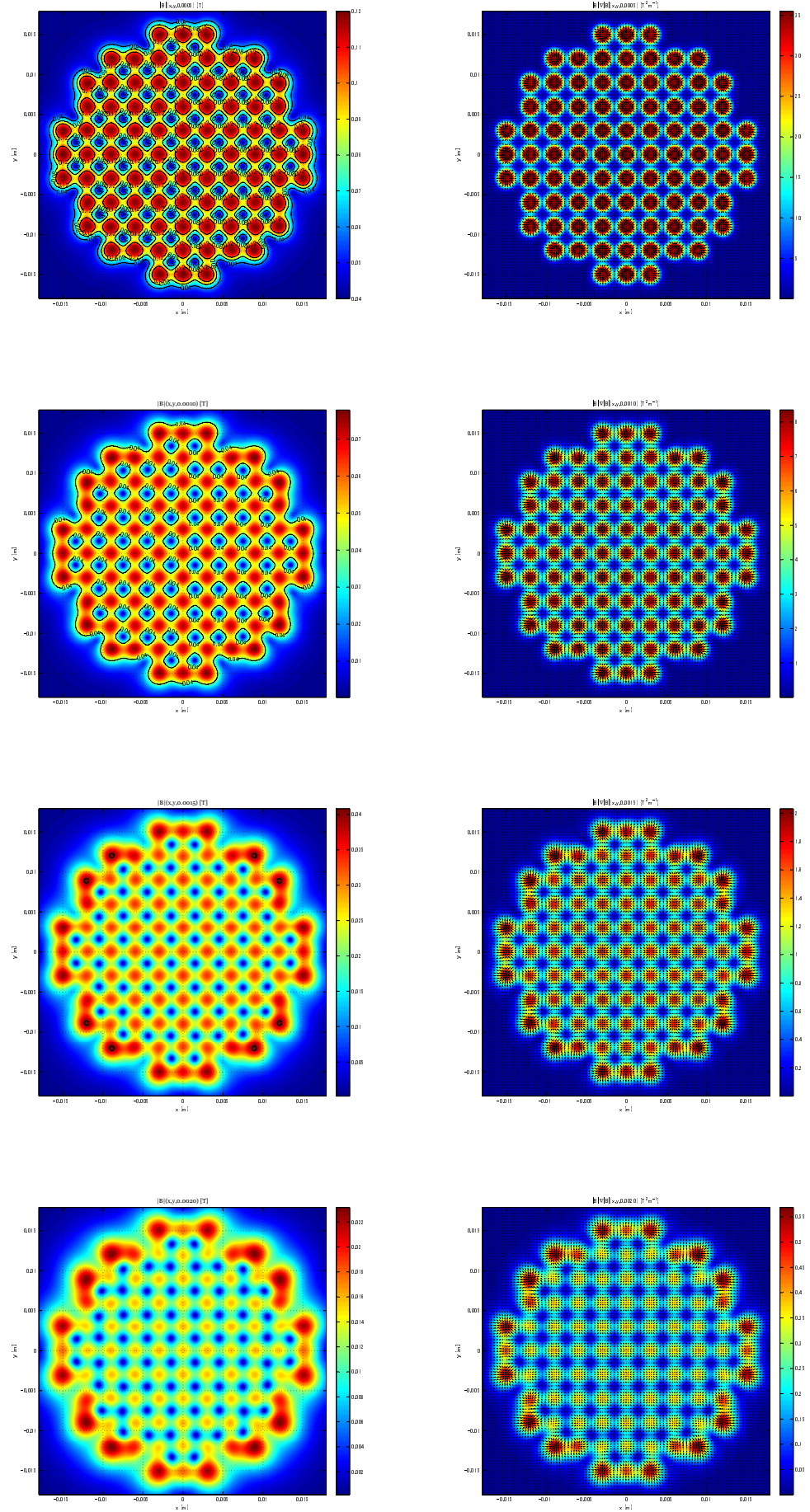


Figure 4.13: Variation of B (left) and ∇B (right) for (a) $z = 0.5$ mm, (b) $z = 1.0$ mm, (c) $z = 1.5$ mm, and (d) $z = 2.0$ mm for a square alternating array. Note that the vertical colour scales are different in each graph.

4.4 Results

4.4.1 Dot deposition

4.4.1.1 Cobalt deposits

For the concentrated Co solution a focussing effect was observed in which there were well defined regions with no Co deposited (fig. 4.15). These regions are the bright white circles e.g. in figure 4.15.c which is the silver substrate showing clearly through the deposit, This decrease in effective area is manifested in the measured deposition current which decreased in the vicinity of complex arrays. Comparison of the calculated magnetic fields (figs. 4.4 -4.11), and the Co deposits (fig. 4.15) indicate that it is the magnetic field ($|\mathbf{B}|$) contours that determine the deposit shape, not ∇B . This is supported by the magnetic field contours imaged using magnetic viewing paper, which closely match the Co deposit morphologies (see fig. 4.16). The most likely explanation for the bald patches is hydrogen accumulation in the interstices. Hydrogen behaves as a diamagnetic vacancy in the paramagnetic cobalt solution and is therefore repelled to the regions of minimum magnetic field gradient. No cobalt deposition is possible in the regions where the surface is occluded by hydrogen.

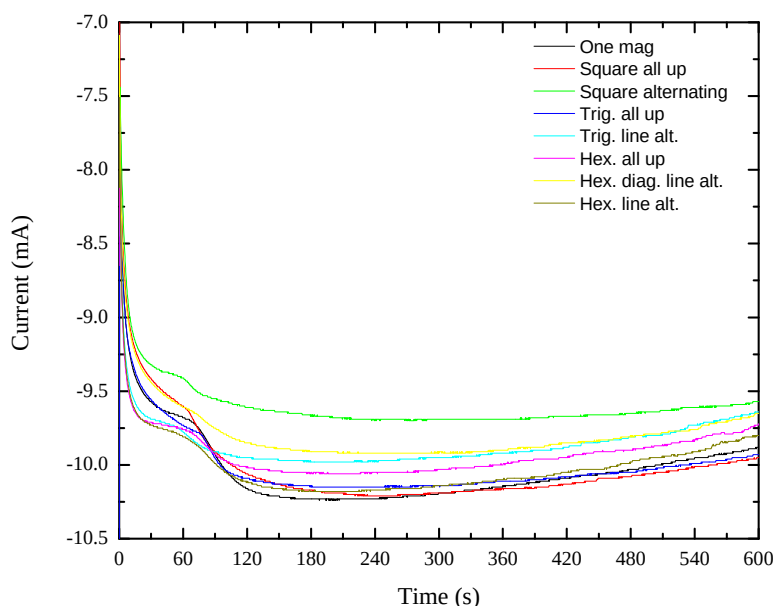


Figure 4.14: Potentiostatic deposition of Co solution, $E = -1.00\text{ V}$ vs. SHE for a selection of magnet arrays.

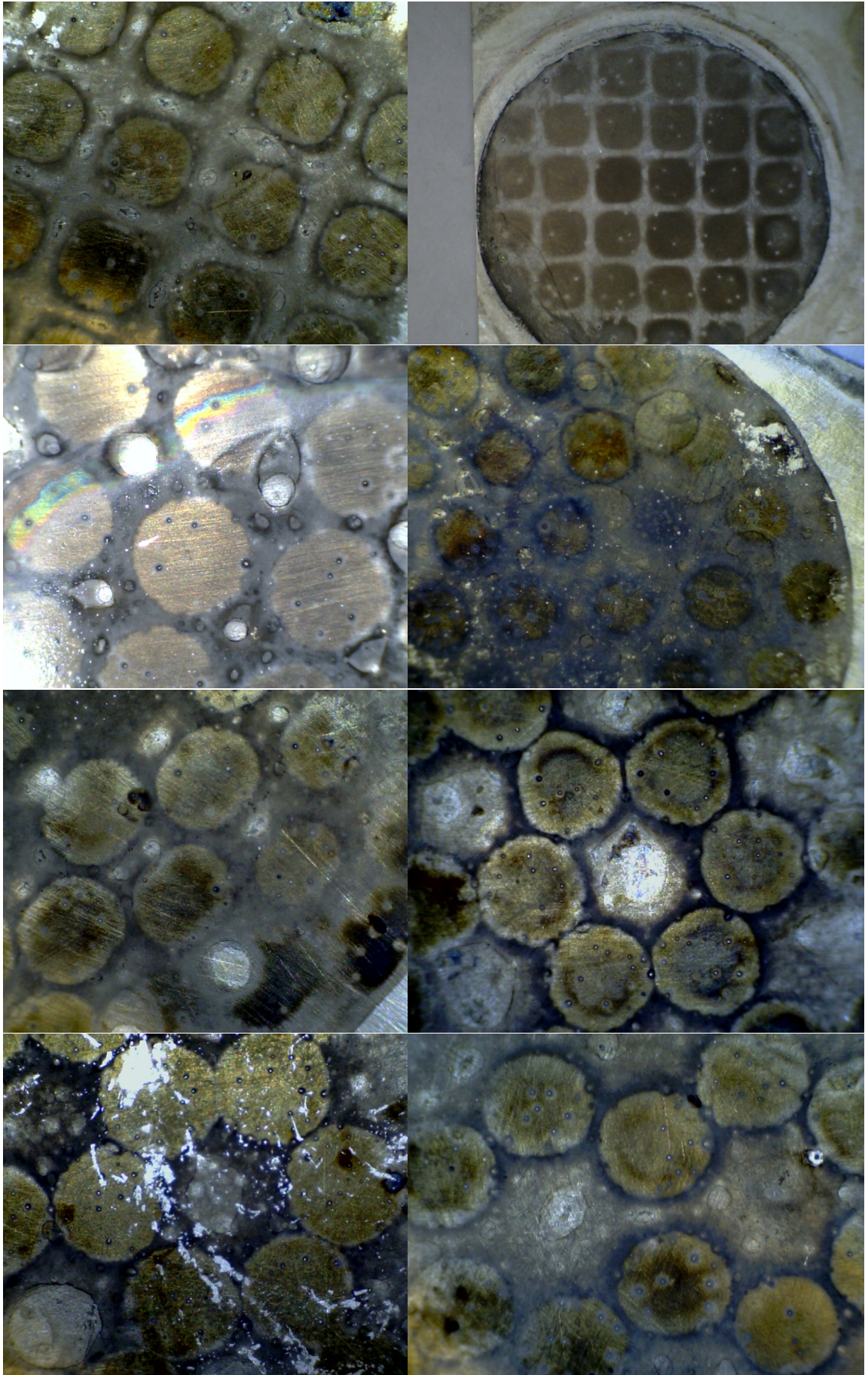


Figure 4.15: Cobalt deposits: (a) Square array all up, (b) square array all up, (c) Square array alternating, (d) Trigonal array all up, (e) Trigonal array line alternating (f) hexagonal array all up, (g) hexagonal array diagonal line alternating, and (h) hexagonal array line alternating.

4. ELECTRODEPOSITION ABOVE PERMANENT MAGNET ARRAYS

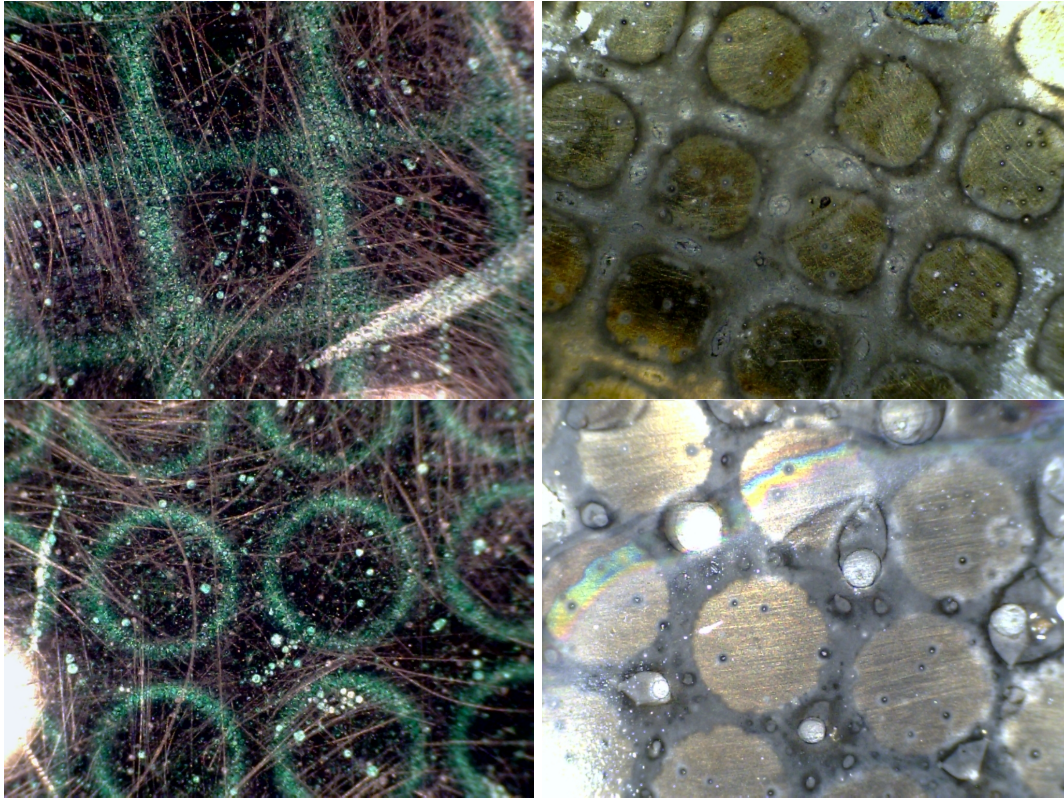


Figure 4.16: Comparison of (a) imposed magnetic field using magnetic viewing film and (b) Co deposit for (top) square array all up, and (bottom) square array alternating.

Table 4.1: $\chi > 0$ Co solution: Influence of array geometry on the current after 200 (s) and 600 (s)

Array	200 (s)		600 (s)	
	I (mA)	% Change	I (mA)	% Change
One mag	-10.2	0.0	-8.5	0.0
Square all up	-10.2	-0.5	-10.0	17.5
Square alternating	-9.7	-5.6	-9.6	13.0
Trig. all up	-10.2	-0.9	-9.9	17.2
Trig. line alt.	-10.0	-2.5	-9.6	13.8
Hex all up	-10.1	-1.8	-9.7	14.8
Hex diag. alt.	-9.1	-3.2	-9.7	13.9
Hex line alt	-10.2	-0.6	-9.8	15.

4.4.1.2 Copper deposits

In contrast, no bald patches were observed for any Cu deposit; a continuous Cu film was deposited in all cases excluding occlusion by trapped bubbles, regardless of bulk susceptibility or array geometry. The molar susceptibility of Cu is almost 10 times smaller than that for Co. Since the field gradient force is also 10 times smaller, we no longer observe a focussing effect, rather a modification of the current distribution. While the total limiting current remains the same, the current distribution is altered by the magnetic field, along with the initial transient current, leading to regions of increased current density, and increased deposition rate (see tables 4.2 and 4.3).

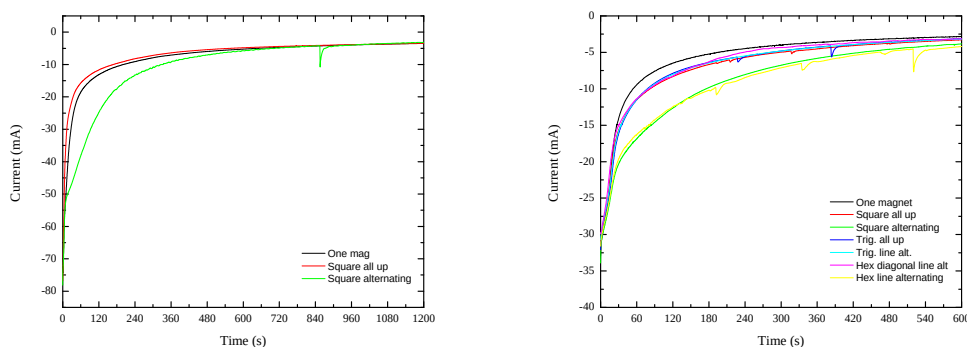


Figure 4.17: Potentiostatic deposition at $E = -0.65$ V vs. SHE for a selection of magnet arrays using (a) $\chi > 0$ Cu solution, and (b) $\chi < 0$ Cu solution.

Table 4.2: $\chi > 0$ Cu solution: Influence of array geometry on the current after 120 (s), 600 (s) and 1200 (s)

Array	120 (s)		300 (s)		1200 (s)	
	I (mA)	% Change	I (mA)	% Change	I (mA)	% Change
One mag	-13.1	0.0	-5.3	0.0	-3.5	0.0
Square all up	-11.7	-11.1	-4.8	-8.0	-3.5	0.0
Square alternating	-24.8	88.8	-5.7	9.0	-3.1	-9.8 ^a

^a Difference due to bubble formation

From Dektak linear scan profiles (fig. 4.18) single magnet dots can be as thick as $55 \mu\text{m}$, dots created above square aligned arrays $\sim 15 \mu\text{m}$, and dots above square alternating arrays $20 - 30 \mu\text{m}$. The current transients, combined with the dektak profiles and optical micrographs clearly show that for weakly paramagnetic systems like Cu the magnetic field gradient force redistributes the current profile, rather than altering the total current.

4. ELECTRODEPOSITION ABOVE PERMANENT MAGNET ARRAYS

Table 4.3: $\chi < 0$ Cu solution: Influence of array geometry on the current after 200 (s) and 600 (s)

Array	300 (s)		1200 (s)	
	I (mA)	% Change	I (mA)	% Change
One magnet	-6.5	0.0	-4.0	0.0
Square all up	-8.3	28.4	-5.0	24.6
Square alternating	-12.6	95.1	-6.8	69.7
Trig. all up	-7.9	2.8	-4.8	20.6
Trig. line alt.	-8.0	23.9	-4.8	20.8
Hex diag. alt.	-8.3	27.5	-4.3	8.5
Hex line alt	-12.5	92.3	-7.1	78.5

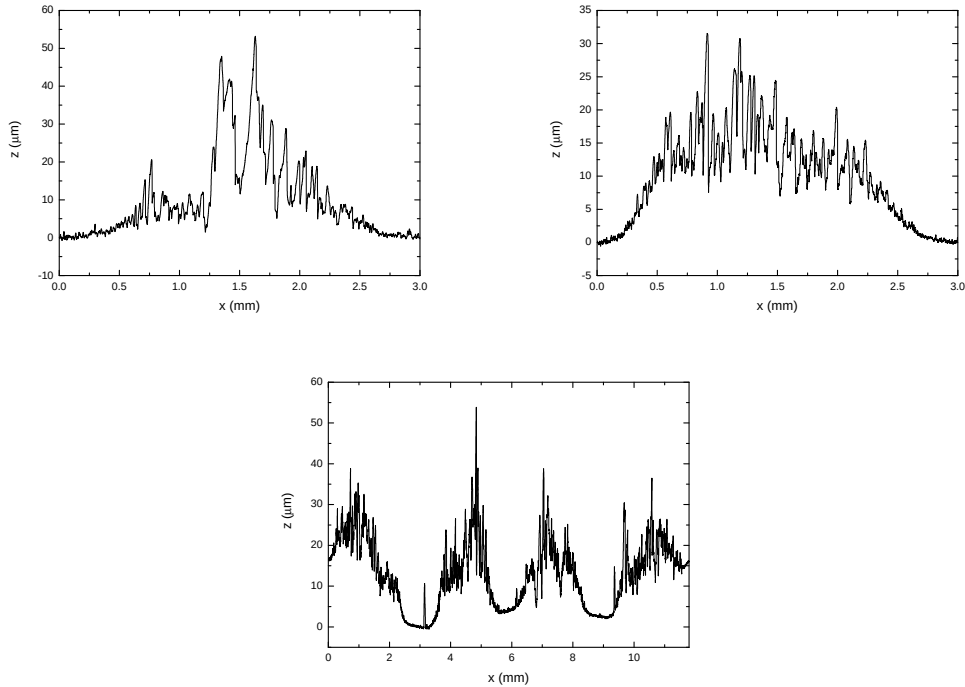


Figure 4.18: Dektak profiles of paramagnetic Cu deposits: (a) above one magnet, (b) detailed profile along one dot above a square array all up, and (c) square array alternating.

One limitation of depositing thin films potentiostatically is that we only measure the total current. We have no unambiguous method to measure the copper deposition and hydrogen currents, and we cannot use an EQCM with the magnet arrays. Instead, by employing galvanostatic methods we can monitor the crossover time from Cu deposition potentials to hydrogen production potentials as we saw in §3.3.3. This gives us a qualitative description of the magnetic force effects on convection in the cell. To further distinguish the bulk or interface nature of the effect a bulk zero susceptibility Cu solution was chosen. For currents ≤ -10 mA, the driving voltage experiences a crossover to a more negative potential as Cu^{2+} ions are depleted close to the electrode surface. In chapter 3 we observed that for Cu deposition at an EQCM an applied magnetic field suppressed the hydrogen evolution reaction by increasing the Cu^{2+} concentration near the electrode surface via the Lorentz force. In the present case, the magnet arrays increase the concentration of Cu^{2+} ions via the field gradient force very close to the electrode surface. This important distinction will be discussed in §4.4.1.3, where it will be shown that the Lorentz force has no effect on the current. Different arrays with different magnetic field strengths and field gradients increase the Cu^{2+} concentration by different amounts, which is exhibited by a change in the crossover time to more negative potentials.

Table 4.4: $\chi = 0$ Cu solution: Influence of array geometry on the voltage crossover time for three currents.

Array	t_c (s)		
	20 mA	15 mA	10 mA
One magnet	104	150	413
Square all up	180	355	~ 600
Square alternating	236	364	> 600
Trig. all up	134	256	462
Trig. line alt.	180		524
Hex. all up	125	189	462

Examining fig. 4.19 and table 4.4 we can see that the most effective arrays for delaying the onset of mass-transport limited Cu deposition are the alternating arrays. These arrays generate the most intense field gradients, so it is reasonable that they exhibit the largest field gradient forces and crossover time changes. At a deposition current of -10 mA a square alternating array can delay the crossover time to 236 s compared to one magnet which has a crossover time of 104 s. The deposition quality is not as good with the bulk zero susceptibility solution, all deposits are dendritic, powdery and have poor adhesion to the substrate. However the bath was not chosen for deposition quality, rather to further highlight that the magnetic field effect is interfacial in nature, and not a bulk effect. Arrays of dots, following $|\mathbf{B}|$ were observed, which is in agreement with the bulk paramagnetic and bulk diamagnetic solutions. This indeed gives greater

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credence to the hypothesis that the ion susceptibility at the electrode surface is the important factor influencing morphology, and not the the bulk susceptibility.

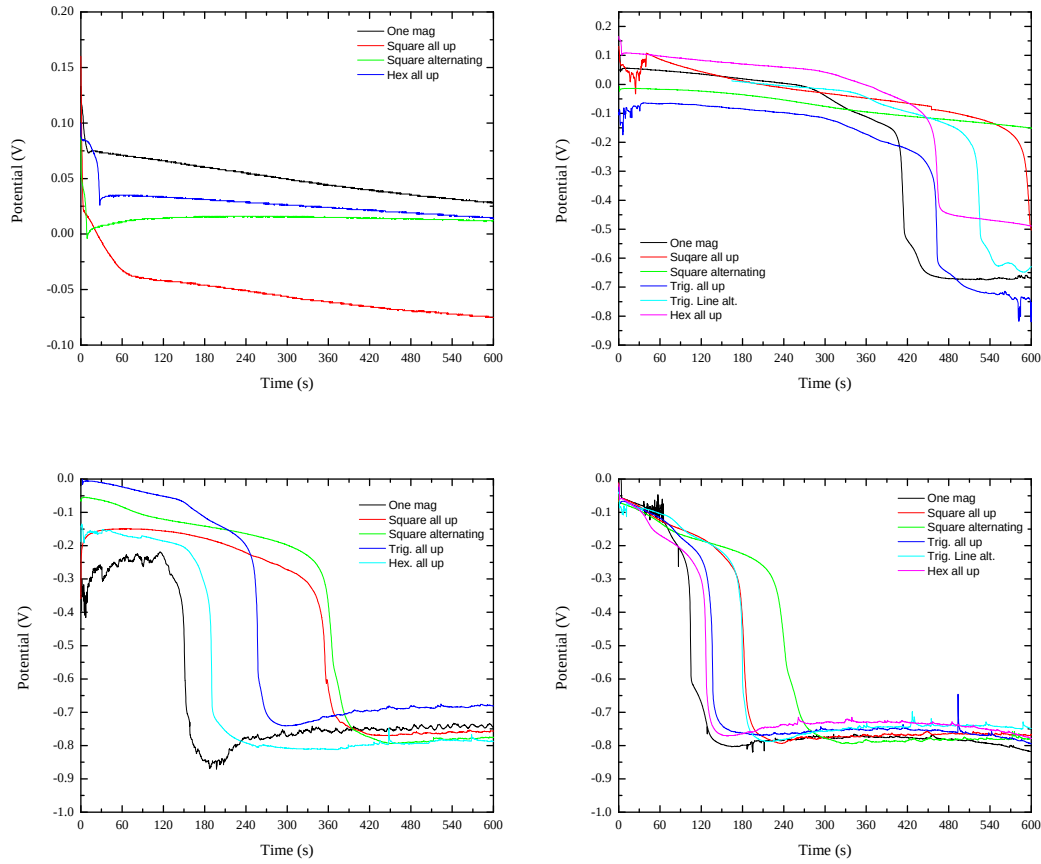


Figure 4.19: Galvanostatic deposition from $\chi \sim 0$ Cu solution at (a) -5 mA, (b) -10 mA, (c) -15 mA, and (d) -20 mA above a variety of magnet arrays.

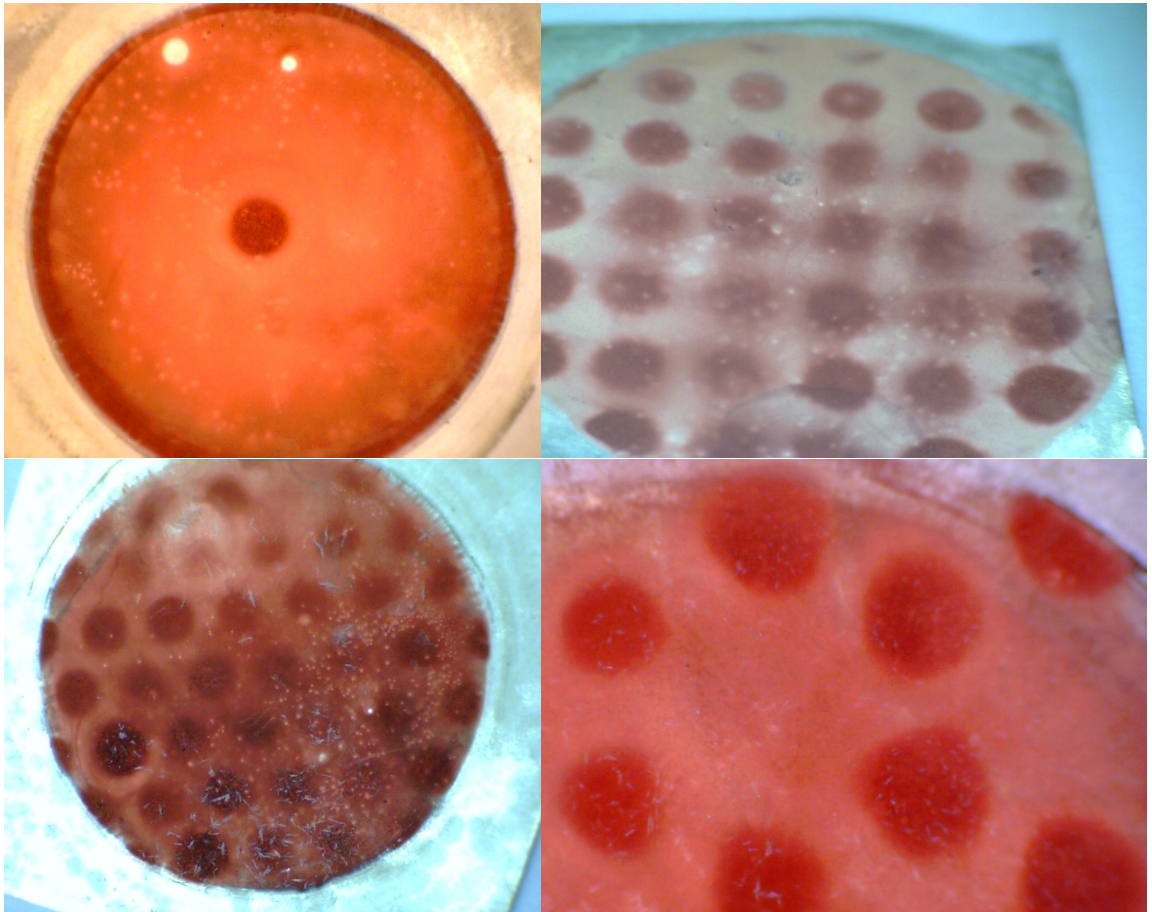


Figure 4.20: $\chi \approx 0$ copper deposits: (a) one magnet, (b) square array alternating (c) trigonal array all up, and (d) hexagonal array all up. Dark regions correspond to thicker Cu deposits.

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4.4.1.3 Eliminating the Lorentz force

Further studies involving the diamagnetic copper solution and two magnets suggest that the field gradient force plays the dominant role. Copper was deposited under four arrangements, (i) parallel magnetisation and a centre-to-centre spacing of 3 mm, (ii) anti-parallel magnetisation and a centre-to-centre spacing of 3 mm, (iii) parallel magnetisation and a centre-to-centre spacing of 6 mm, and (iv) anti-parallel magnetisation and a centre-to-centre spacing of 6 mm.

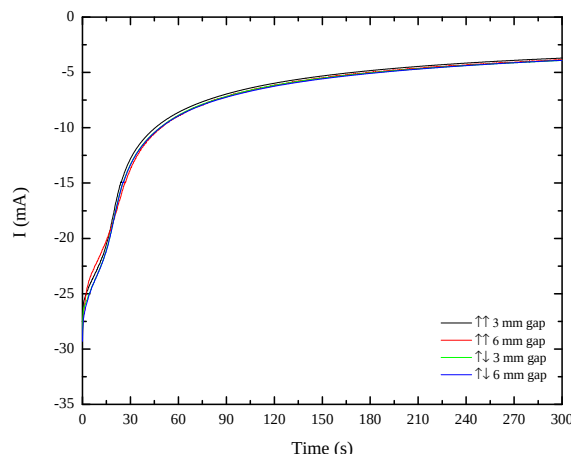


Figure 4.21: Potentiostatic deposition of Cu above four magnet arrangements.

If the Lorentz force dominated the deposition current, then it would be expected that arrangements (ii) and (iv) would exhibit an increased deposition rate due to a more intense local flow (see fig. 4.2). Instead figure 4.21 shows that there was little, if any, effect on the deposition current for the four magnet arrangements. The differences in current magnitude can be attributed to bubble formation from poor seals which decrease the effective surface area.

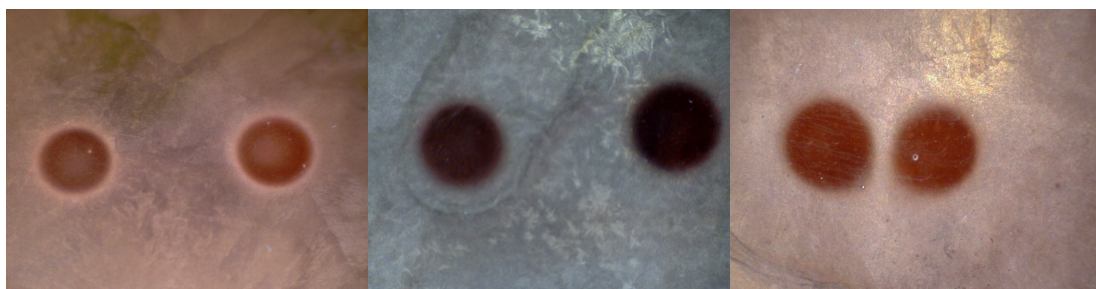


Figure 4.22: Cu deposits above (a) two aligned magnets with a centre to centre distance of 6 mm, and two alternately magnetised magnets with a centre to centre distance of (b) 6 mm and (c) 3 mm.

4.4.1.4 Natural Convection

The inverted working electrode cell design was chosen to minimise the effects of natural convection, as outlined in §4.2. Here we present data showing the rationale for this choice. In contrast to the previous cell the working electrode is upright and can be freely influenced by natural convection (fig. 4.23).

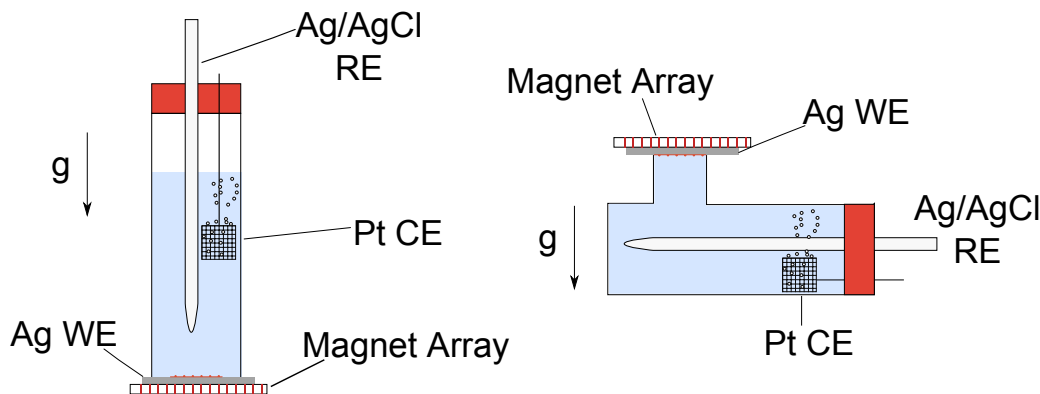


Figure 4.23: Comparison of working electrode orientation: (a) upright working electrode; experiences fluid flows due to natural convection and (b) inverted working electrode, which minimises natural convection effects.

As discussed in §4.3.1, the magnetic field decays as z^{-3} so three foil thicknesses were used to see if varying the magnetic field strength would alter the deposit geometry in the presence of natural convection. The three foils used were (i) $100\mu\text{m}$ Cu foil, (ii) $50\mu\text{m}$ Ag foil, (iii) $7\mu\text{m}$ Cu foil. Cu was deposited potentiostatically at -0.1 V , and at -0.15 V for 300 s. Smooth films were deposited at -0.1 V , (fig. 4.24.a, c, d), and the maximum height recorded was 500 nm by a Dektak profilometer (fig. 4.25.a) for a square alternating array. At larger potentials (-0.15 V) dendritic deposits were formed, and a clustering effect was observed rather than dot deposition (fig 4.24.b & fig. 4.25.b). Decreasing the film thickness from $100\mu\text{m}$ to $7\mu\text{m}$ made no appreciable difference to surface morphology, indicating that even for more intense magnetic field gradient forces, it is not large enough to overcome disruption by natural convection.

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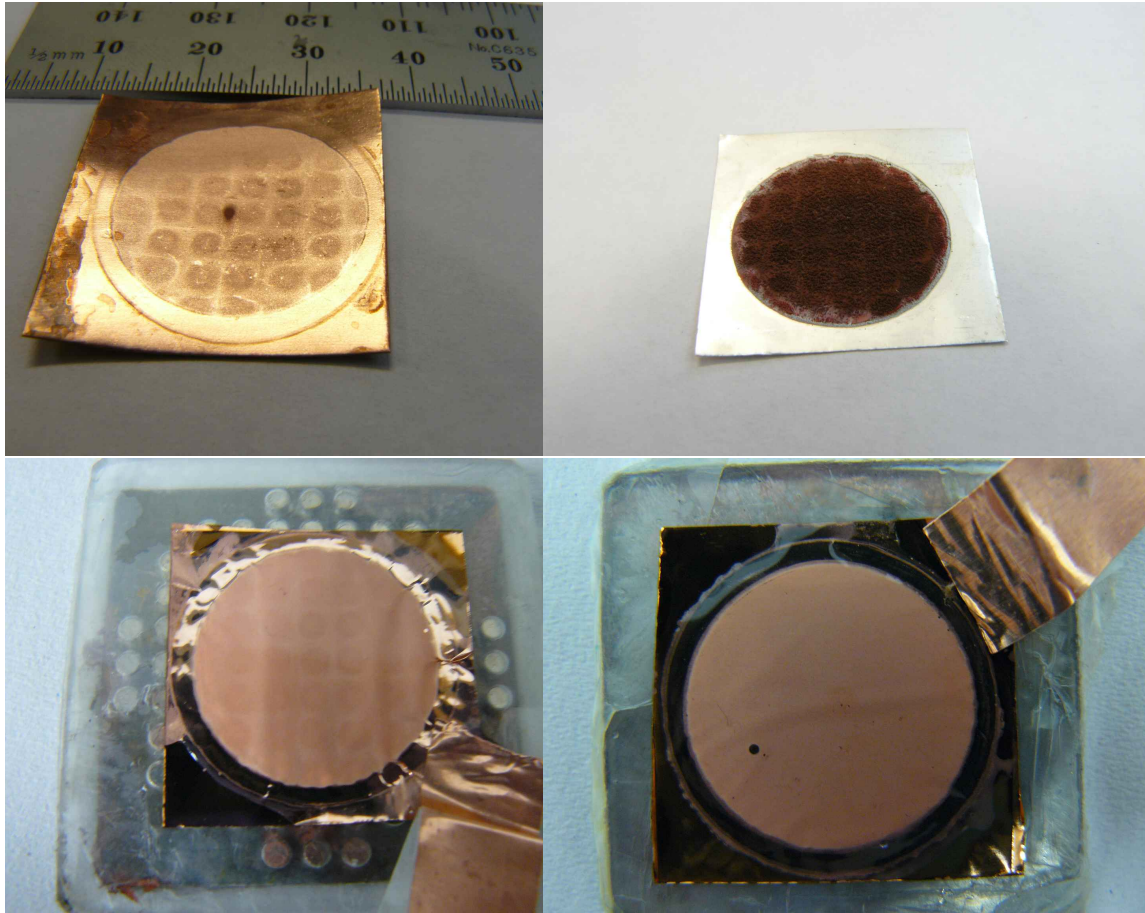


Figure 4.24: Cu deposits at upright working electrode electrodes (a) square alternating array on $100\mu\text{m}$ thick Cu foil, (b) square alternating array on $50\mu\text{m}$ Ag foil, (c) square alternating array on $7\mu\text{m}$ thick Cu foil, and (d) one magnet, on $7\mu\text{m}$ thick Cu foil.

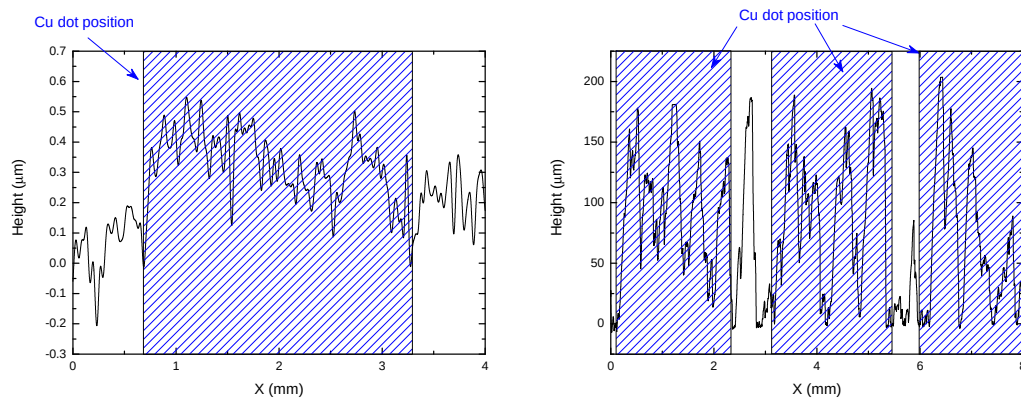


Figure 4.25: Dektak profilometer scans of (a) a Cu dot on $100\mu\text{m}$ Cu foil above a square alternating array, and (b) a series of dots in a dendritic deposit on a $50\mu\text{m}$ Ag foil above a square alternating array. The blue hatch lines indicate the location of the dot.

4.4.2 Anti-dot deposition

4.4.2.1 Zn deposition

So far we have shown that it is possible to use patterned magnetic fields to deposit arrays of dots, the question that now arises, is it possible to use diamagnetic ions to deposit anti-dots? Diamagnetic Zn was deposited on Ag foils in proximity to various array configurations. The bath used was 0.1 M ZnCl_2 + 0.6 M H_3BO_3 ; Zn films were deposited galvanostatically at -10 mA for 600 s, with the substrates facing downwards to mitigate any effects from natural convection. No effect was observed on surface morphology for any array combination.

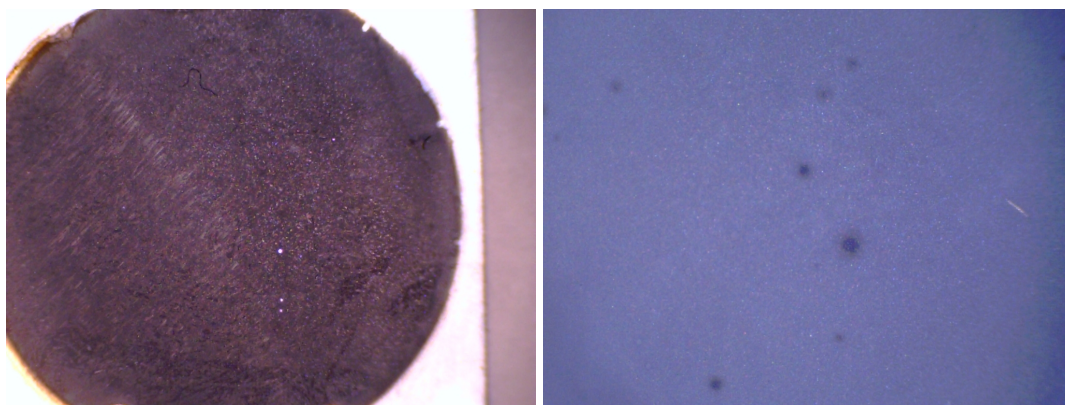


Figure 4.26: Zn deposition above a square alternating array; no effect was observed.

Zn was chosen as it is diamagnetic in both its metal state, and as an ion in solution. Zn^{2+} is a $3d^{10}$ ion, and so has no unpaired spins, and a susceptibility of $-1.4 \cdot 10^{-10} \text{ m}^3 \text{ mol}^{-1}$, which is two orders of magnitude smaller than that of Cu^{2+} ions, and almost three orders of magnitude smaller than Co^{2+} (see table 2.1). In a plane 0.5 mm above a square alternating array, the maximum $B\nabla B$ is $\sim 35 \text{ T}^2 \text{ m}^{-1}$, the molar susceptibility of Zn is $\chi_m = -1.6 \cdot 10^{-10} \text{ m}^3 \text{ mol}^{-1}$, and the ion concentration was 0.1 mol l^{-1} , leading to a field gradient force of -0.2 N m^{-2} , which is much smaller than the force due to natural convection (table 2.3). Clearly the magnetic field gradient force acting on diamagnetic ions is not large enough to overcome natural convection in an electrochemical cell. As seen in §4.4.1.4 natural convection plays an important role in electrodeposition. It can disrupt pattern deposits for paramagnetic ions such as Cu in non-ideal electrode alignments, and prevents the formation of diamagnetic Zn dots for any arrangement of magnets. This also provides us with an extra argument against a Lorentz force effect, since there were moving ions in solution, but no pattern was observed.

4.4.2.2 Rare-Earth Paramagnetic Solutions

Another approach must be found to realise inverse magnetic templating, and we revisit the field gradient force example in §2.5. In highly paramagnetic liquids such as

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concentrated $\text{Dy}(\text{NO}_3)_3$ solutions, less paramagnetic material can act as diamagnetic voids [16], and the balance between the field gradient and buoyancy forces creates levitation conditions that are possible with conventional electromagnets. The levitation condition is described by the product of $B\nabla B$ required to levitate an object in solution

$$B\nabla_z B = \frac{(\rho - \rho_{sol})}{(\chi - \chi_{sol})} \mu_0 g \quad (4.1)$$

where ρ and ρ_{sol} are the density of the object and solution respectively, μ_0 is the permeability of free space, and χ and χ_{sol} are the dimensionless susceptibilities of the object and solution respectively. As seen in figure 4.27 it is possible to levitate C, Si, and Ti in a concentrated $\text{Dy}(\text{NO}_3)_3$ solution in the fringing field of a 1.5 T electromagnet.

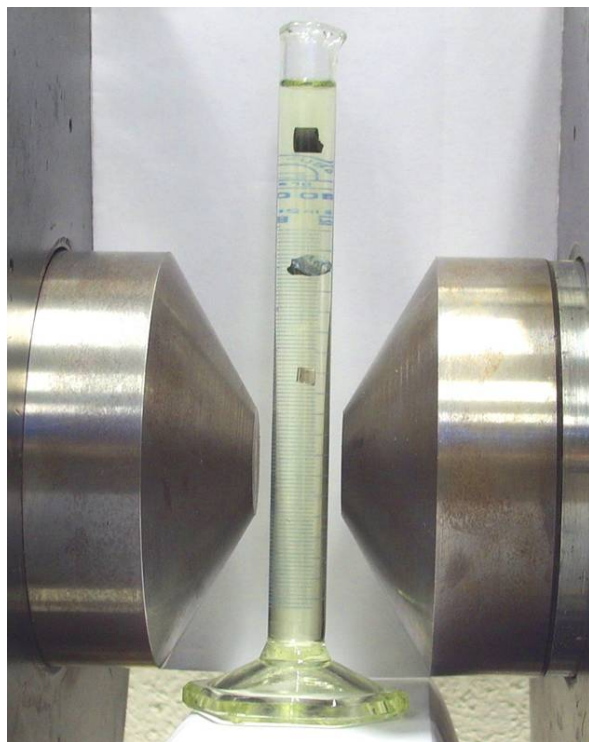


Figure 4.27: From top to bottom, C, Si, and Ti levitating in a 2.67 M $\text{Dy}(\text{NO}_3)_3$ solution in the fringing field of a 1.5 T electromagnet. [16]

Using this as the inspiration for an inverse template, the effective diamagnetic susceptibility of any ion in solution close to the electrode surface will be similar in magnitude to the susceptibility of the paramagnetic Dy solution, and so it would be expected that the field gradient force should be large enough to induce anti-dot deposition. Two different baths were used to study this effect, the first consisted of 1 M $\text{Dy}(\text{NO}_3)_3$ + 0.1 M CuSO_4 + 0.3 M H_3BO_3 , and the second contained dysprosium and copper salts with the same dimensionless susceptibility: 3.3 mM $\text{Dy}(\text{NO}_3)_3$ + 0.1 M CuSO_4 + 0.3 M H_3BO_3 .

$\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ has a mass susceptibility of $1.25 \cdot 10^{-6} \text{ m}^3 \text{ kg}^{-1}$ (fig. 4.28.a), and using concentrated $\text{Dy}(\text{NO}_3)_3$ solutions, dimensionless susceptibilities as high as 10^{-3}

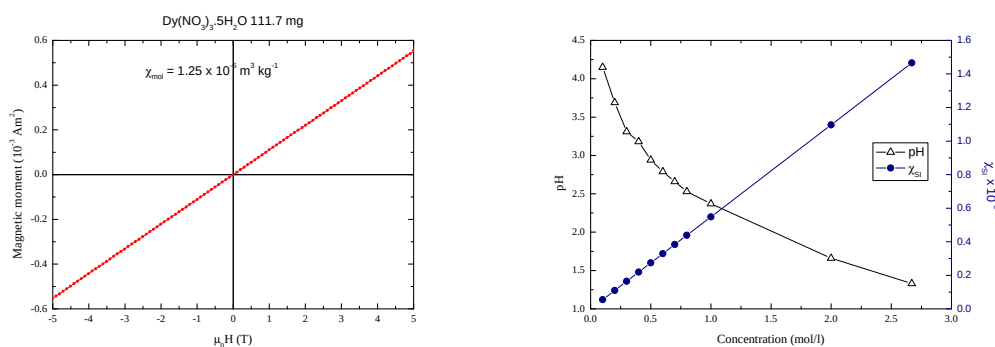


Figure 4.28: Susceptibility for (a) polycrystalline $\text{Dy}(\text{NO}_3)_3$, and (b) $\text{Dy}(\text{NO}_3)_3$ solutions.

are possible (fig. 4.28.b). Even at high concentrations the susceptibility is linear with density, and the demagnetising field is negligible, meaning that there is no concentration gradient correction to the force experienced by the solution, i.e., the Kelvin force is still applicable rather than the Helmholtz force (§2.5).

The benefit of using aqueous dysprosium salt solutions is that the Dy^{3+} reduction potential (see fig. 4.29) is a lot more negative than that for Cu^{2+} (-0.340 V). Therefore at low voltage deposition conditions, dysprosium is unlikely to deposit, which is important in the realisation of inverse template deposition. If dysprosium did deposit at these low potentials there would be a measurable amount deposited in high magnetic field regions using the magnet arrays.

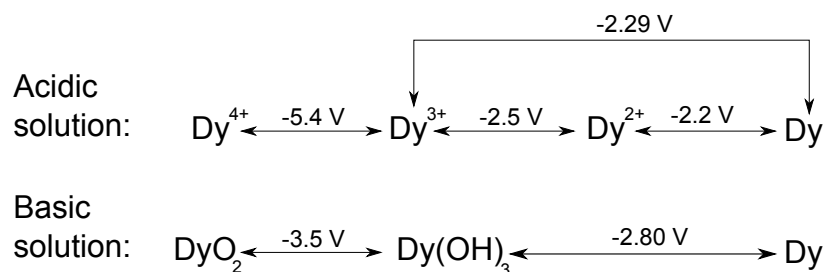
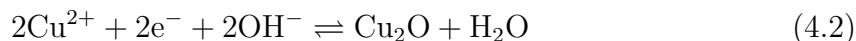


Figure 4.29: Standard potentials for dysprosium reduction in acidic and basic solutions (values from [17]).

For all arrays tested, Cu deposits formed which followed an inverse pattern to those from the previous section (fig. 4.33). In high magnetic field regions, Cu deposition was suppressed due to the attraction of Dy^{3+} ions to the electrode surface, and the Cu deposited as sparse cubic crystals. Large concentrations of oxygen were detected using EDX analysis (figs. 4.34 and 4.35, tables 4.6 and 4.7), and we conclude that the deposit is a copper oxide such as Cu_2O rather than Cu metal. This is unusual as the solution has a pH of 2.4 (fig. 4.28.b), and from the Pourbaix diagram of Cu we know that Cu_2O is thermodynamically unstable outside the pH range 6-14 in aqueous environments [18]. Other studies have shown that the local pH at electrode surfaces can increase under applied magnetic fields [19, 20] when the hydrogen evolution reaction is

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mass transport limited. They concluded that the effect was due to the Lorentz force, with a possible, but minimal influence of the field gradient force close to the electrode surface on diamagnetic hydrogen gas. However, as shown in §4.4.1.2, the Lorentz force has minimal effect on the Cu deposition current, and it is the field gradient force that influences the current distribution. Since the Dy solution is very paramagnetic all other ions in solution act as diamagnetic voids, including H^+ and Cu^{2+} ions. In this situation, all H^+ ions and H_2 gas will be expelled from regions of high magnetic field by the Dy^{3+} ions, thereby increasing the local pH, and favouring oxide or hydroxide deposition and precipitation such as:



This contrast with the regions of low magnetic field, where Cu deposition is no longer inhibited by Dy^{3+} ions and dense dendritic deposits are formed (fig. 4.42). The dendritic growth is a signature of mass transport limited deposition [17], and there is significantly less oxygen in the deposits (tables 4.6 and 4.7) suggesting that the pH remains lower in these regions.

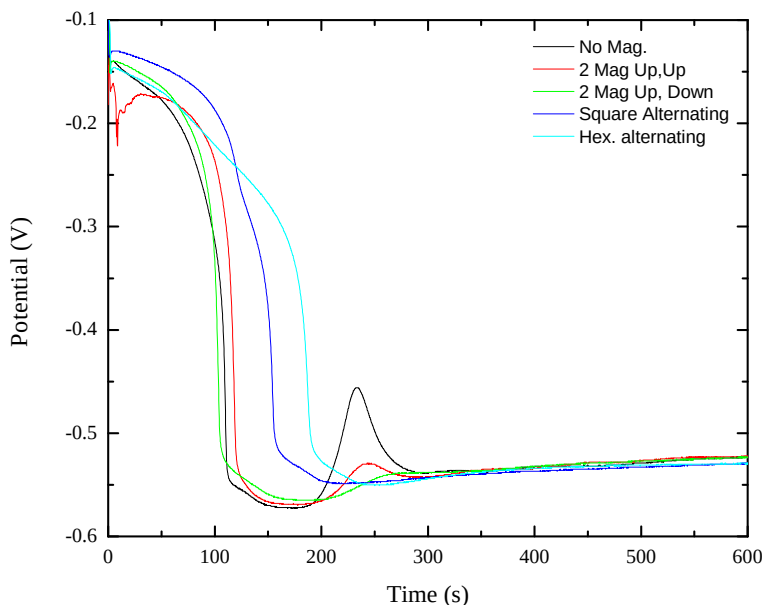
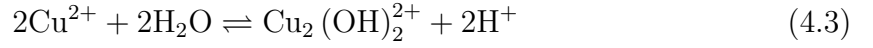


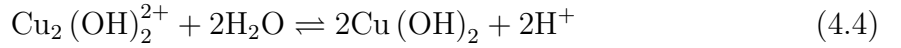
Figure 4.30: Galvanostatic deposition of Cu in paramagnetic $Dy(NO_3)_3$ solution above a series of magnet arrays.

Similar to the previous results on the galvanostatic deposition of Cu from bulk $\chi = 0$ solutions, the crossover time was delayed the most by alternating arrays (fig. 4.30 and table 4.5). Looking at the zero field voltage transient, one interesting feature is the brief drop in potential after the voltage has already shifted to more cathodic currents. Initially the voltage becomes more cathodic to maintain the current as more Cu^{2+} ions are depleted from the electrode surface. At more cathodic values depletion of H^+ ions

increases, which causes an increase in pH, thus the hydrolysis of the metal ion becomes possible [20]:



The metal hydrolysis decreases the pH once again, and Cu metal deposition continues (see fig. 4.31). With the application of patterned magnetic fields the trough at ≈ 240 s is suppressed with more intense magnetic field gradient patterns. As stated previously, in the presence of a magnetic field the local pH increases as H^+ is removed from solution. This drives the Cu reaction towards metal hydration almost exclusively, and once the pH becomes large enough it is possible for copper hydroxide or copper oxide to precipitate out of solution



thus supporting the observation of the formation copper oxide or hydroxide deposits in the presence of patterned magnetic fields.



Figure 4.31: Optical micrograph of Cu deposited from the concentrated $\text{Dy}(\text{NO}_3)_3$ without an external magnet field.

Table 4.5: Crossover voltage times for Cu deposition in concentrated $\text{Dy}(\text{NO}_3)_3$ solutions.

Array	T_c (s)
None	106
2 aligned	115
2 alternating	101
Square alternating	149
Hexagonal alternating	186

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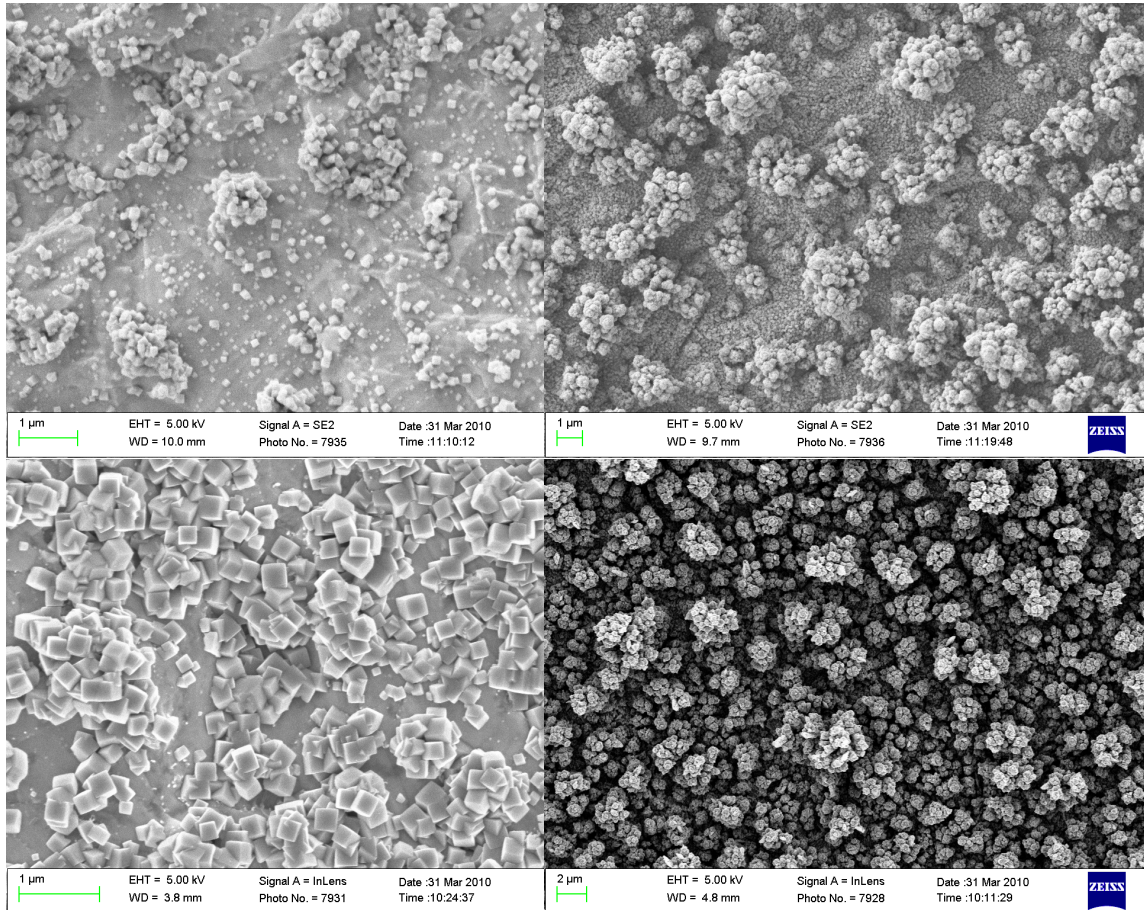


Figure 4.32: SEM micrographs of Cu deposits in concentrated $\text{Dy}(\text{NO}_3)_3$ solutions: above one magnet (a) above the magnet (high field), and (b) away from the magnet (low field); above an aligned hexagonal array (c) high field, and (d) low field.

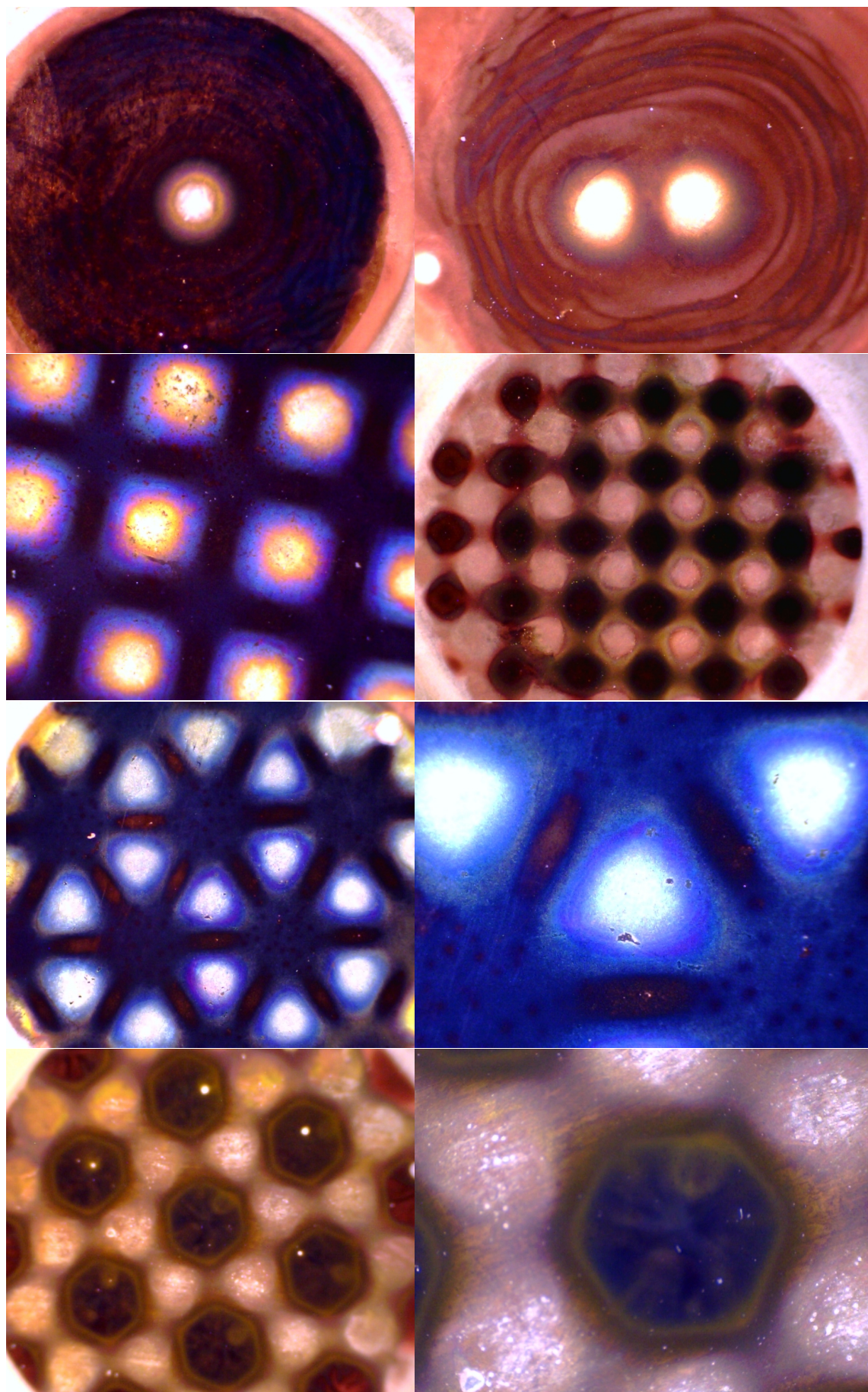


Figure 4.33: Cu deposits in concentrated $\text{Dy}(\text{NO}_3)_3$ solutions: (a) one magnet, (b) two magnets aligned, (c) square array all up, (d) square array alternating, (e & f) hexagonal array all up, (g & h) hexagonal array diagonal line alternating. Light regions correspond to the Ag substrate, dark regions are $\text{Cu}/\text{Cu}_y\text{O}_x$ deposits.

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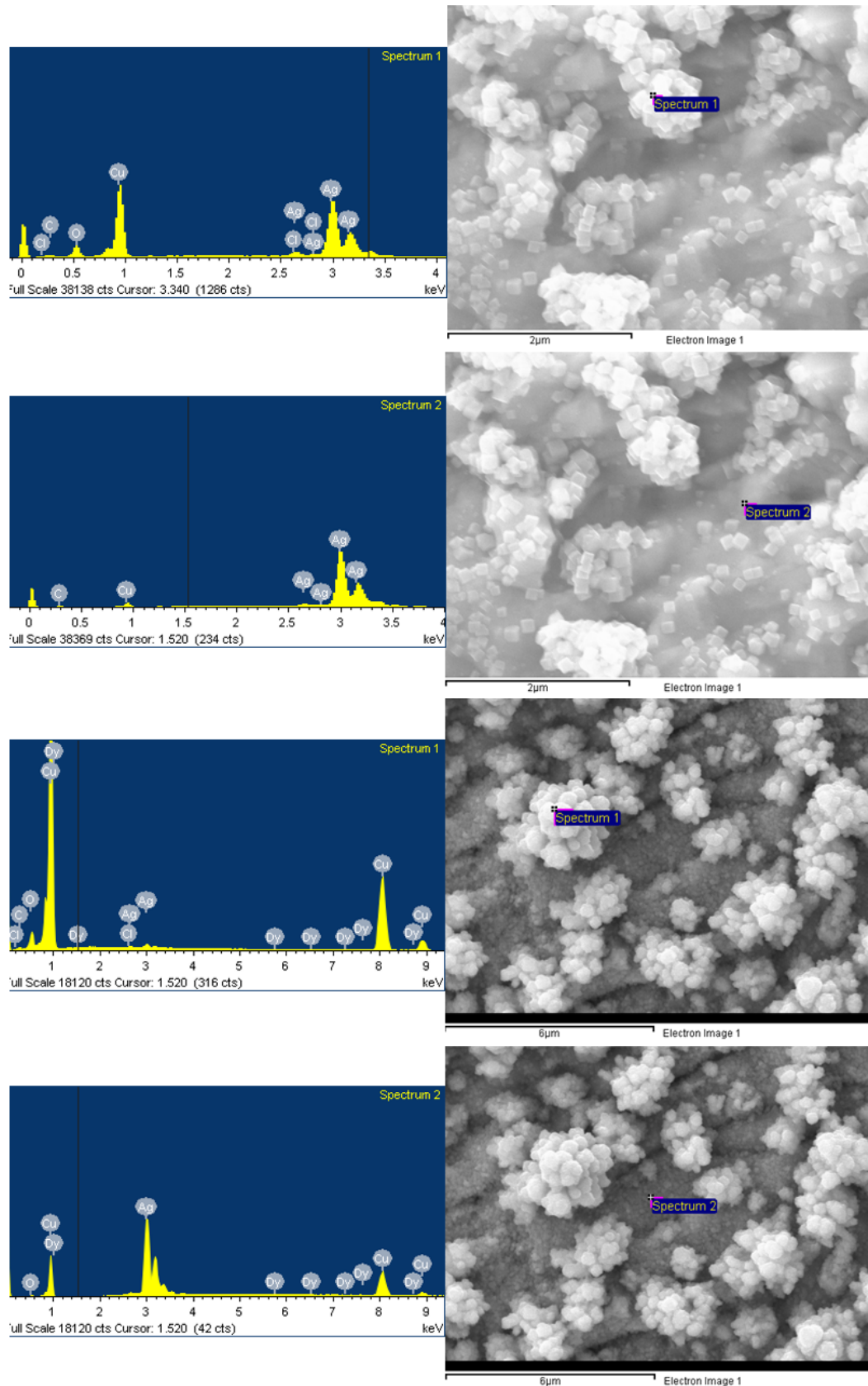


Figure 4.34: EDX elemental analysis of Cu deposits from concentrated $\text{Dy}(\text{NO}_3)_3$ at (a) one magnet, high field, (b) one magnet, high field, substrate, (c) one magnet, low field, and (d) one magnet, 1 field, substrate. Panels on the left are the EDX spectra, panels on the right are SEM images indicating where the EDX spectra were taken.

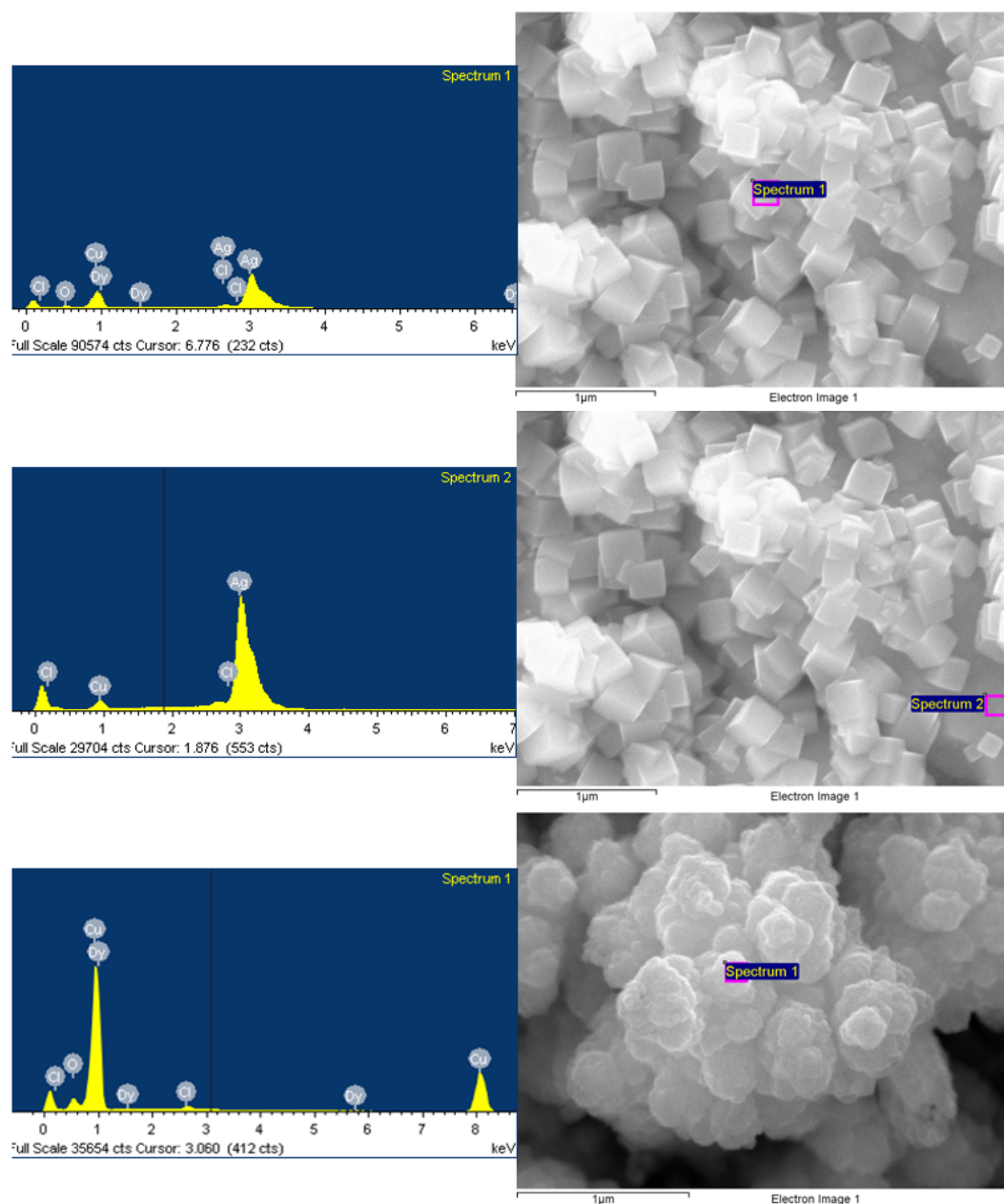


Figure 4.35: EDX elemental analysis of Cu deposits from concentrated $\text{Dy}(\text{NO}_3)_3$ at (a) aligned hexagonal array, high field, (b) aligned hexagonal array, high field, substrate, and (c) aligned hexagonal array, low field. Panels on the left are the EDX spectra, panels on the right are SEM images indicating where the EDX spectra were taken.

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Table 4.6: EDX elemental analysis of Cu deposits in the concentrated $\text{Dy}(\text{NO}_3)_3$ solution above one magnet.

Element	Edge	Large B		Small B	
		Base		Base	
		Atomic %	Atomic %	Atomic %	Atomic %
C	K	619	4.7	16.1	-
O	K	55.4	16.8	21.1	13.1
Cl	K	0.9	-	0.4	47.3
Cu	K	18.4	3.0	61.5	39.6
Ag	L	19.3	75.5	0.8	0.1
Dy	L	-	-	0.01	-
Total		100	100	100	100

Table 4.7: EDX elemental analysis of Cu deposits in the concentrated $\text{Dy}(\text{NO}_3)_3$ solution above an aligned hexagonal array.

Element	Edge	Large B		Small B
		Base		
		Atomic %	Atomic %	Atomic %
C	K	-	-	-
O	K	51.6	-	36.6
Cl	K	1.6	1.1	2.3
Cu	K	14.1	4.9	61.0
Ag	L	32.8	94.0	-
Dy	L	0	0	0
Total		100	100	100

4.4.2.3 Balanced Cu-Dy Susceptibility Solution

The dimensionless susceptibility of 3.33 mM $\text{Dy}(\text{NO}_3)_3$ is the same as 0.1 M CuSO_4 . For a solution of this composition, in the presence of a magnetic field gradient, equal numbers of Dy^{3+} and Cu^{2+} ions may be expected to collect in the region of highest magnetic field. Deposition was carried out under the same conditions as the concentrated $\text{Dy}(\text{NO}_3)_3$ solution, i.e. galvanostatically at -10mA for 10 minutes. Cu deposition is strongly inhibited by the presence of equal amounts of Cu and Dy at the electrode surface, and the voltage is pushed significantly further negative to drive the same current. This is clear by comparing the balanced susceptibility voltage transients to those of the concentrated solution. Similar to the concentrated solution (fig. 4.30); the strongest voltage response modification is by the arrays which generate the largest and most intense magnetic field gradients, the alternating arrays. Inspection of the deposits by SEM and optical methods also show an inhibition of metal deposition. Dendritic structures form in regions of large magnetic field, and suppressed columnar growth is observed in regions of low magnetic field. EDX elemental analysis suggest that the deposits are primarily copper oxide or copper hydroxide, which can be explained by a local increase in pH by the same mechanism as the concentrated solutions. This is further supported by the lack of copper oxide deposition under no applied field. When there are no magnetic field gradients the Dy^{3+} ions are not attracted to the electrode surface, and Cu deposition is no longer inhibited (see fig. 4.37.a). Further evidence for this is in the potential transient. The potential remains at a much smaller value than what is required with the application of a magnetic field gradient.

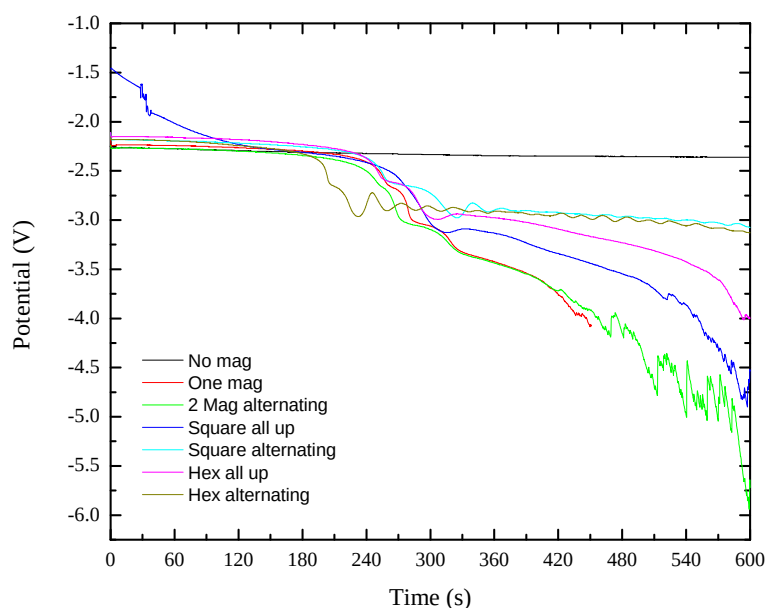


Figure 4.36: Galvanostatic deposition of Cu in balanced susceptibility $\text{Dy}(\text{NO}_3)_3$ solution above a series of magnet arrays.

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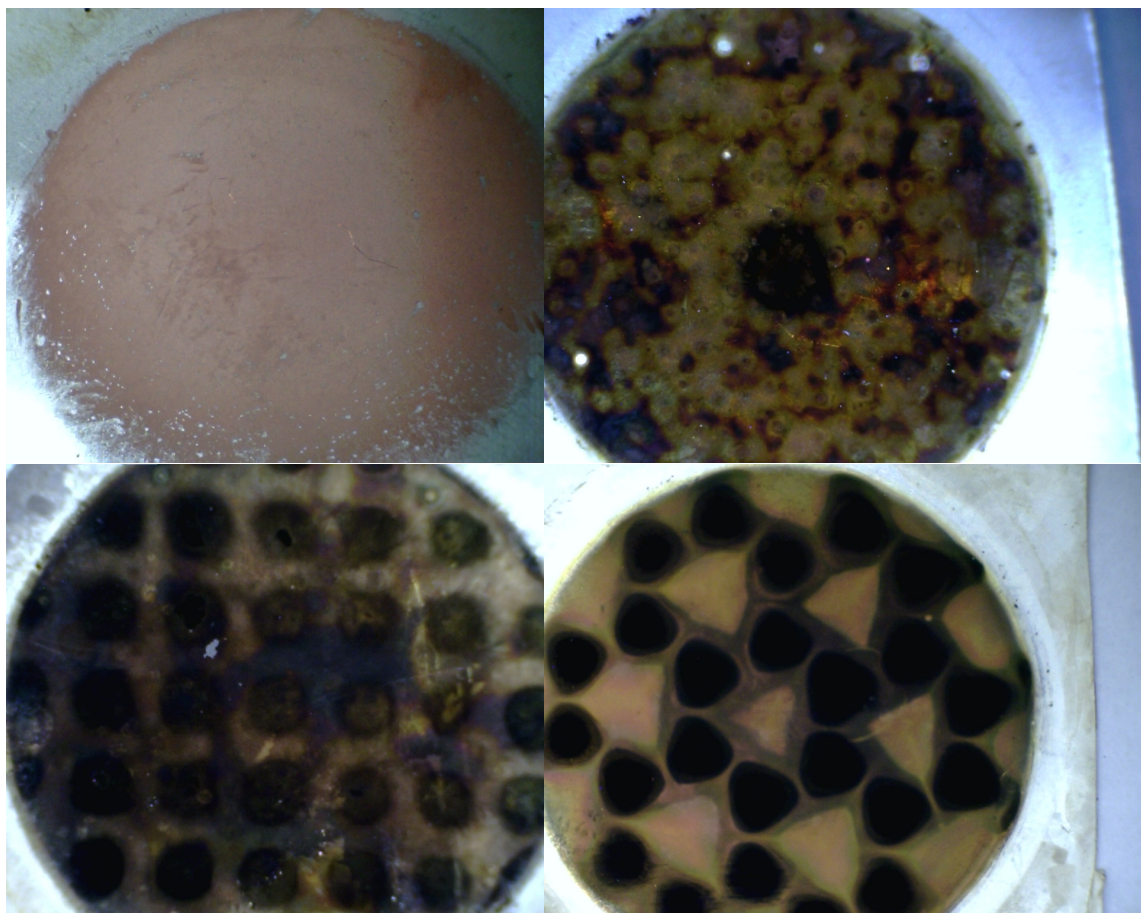


Figure 4.37: Optical micrographs of Cu deposition from the 3.3 mM $\text{Dy}(\text{NO}_3)_3$ solution for (a) no magnet, which exhibits a uniform Cu metal deposit, (b) one magnet, (c) square alternating array, and (d) aligned hexagonal array. Black regions correspond to thicker Cu_yO_x deposits

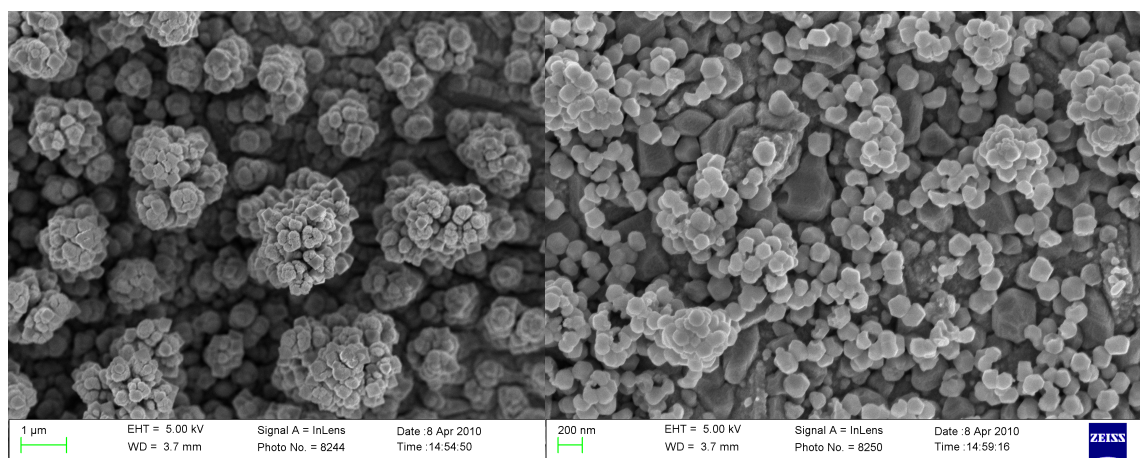


Figure 4.38: SEM micrographs of Cu deposits from balanced susceptibility $\text{Dy}(\text{NO}_3)_3$ solution at an aligned hexagonal array: (a) high field, and (b) low field.

Table 4.8: EDX elemental analysis of Cu deposits from balanced susceptibility $\text{Dy}(\text{NO}_3)_3$ solution at an aligned hexagonal array.

Element	Edge	Large B		Small B	
		Atomic %	Base	Atomic %	Base
C	K	10.0	-	-	-
O	K	24.7	21.2	39.3	36.8
Cl	K		-	1.4	-
Cu	K	65.0	54.1	59.3	7.2
Ag	L	0.3	24.7		56.0
Total		100	100	100	100

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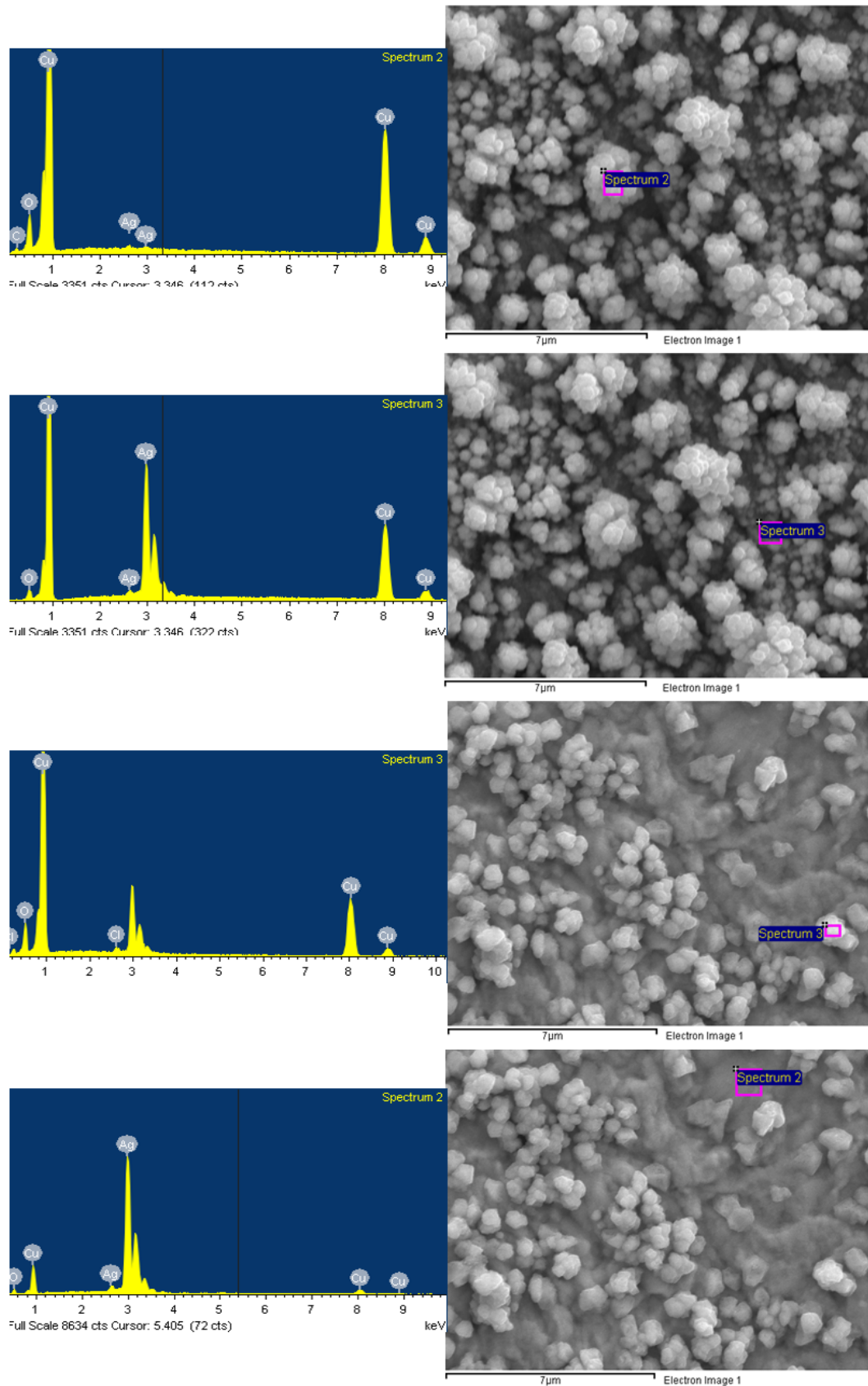


Figure 4.39: EDX elemental analysis of Cu deposits from balanced susceptibility $\text{Dy}(\text{NO}_3)_3$ solution at an aligned hexagonal array, (a) high field, (b) high field substrate, (c) low field, and (d) low field substrate. Panels on the left are the EDX spectra, panels on the right are SEM images indicating where the EDX spectra were taken.

4.4.2.4 Dysprosium Oxide Deposition

During the deposition of Cu in the balanced susceptibility solutions in the vicinity of a permanent magnet array the potential decreases to values that allow the deposition of Dy to occur (compare figs. 4.36 and 4.29). In regions of high magnetic field dark dysprosium deposits were formed. When exposed to air the deposits underwent an oxidation to a grey-white material. EDX analysis confirm the presence of dysprosium and a considerable amount of oxygen (see fig. 4.42 and table 4.9), and are possibly Dy_2O_3 or $\text{Dy}(\text{OH})_3$. The Dy deposits were observed to deposit only in regions of high magnetic field, where Dy^{3+} ions are strongly attracted to the electrode surface. For deposition to occur only above the magnets the magnetic field must lower the energy barrier for deposition. The Zeeman splitting of spin up and spin down electronic states ($= 2\mu_B\mathbf{B}$) in a 1 T field is $\approx 1.2 \cdot 10^{-4} \text{ eV}$, which is significantly smaller than the Gibb's free energy of the Cu^{2+} deposition. As noted in 3.3.1, the standard potential for the reaction $\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}$ is $E^0 = 0.337 \text{ V vs. SHE}$. The Gibb's free energy is

$$\Delta G = -nFE^0 = 65 \text{ kJ mol}^{-1} \quad \text{or} = 0.7 \text{ eV per ion} \quad (4.5)$$

thus ruling out a direct magnetic field effect on the kinetics of the system. Since we know that the Dy^{3+} concentration has increased at the electrode surface one possible explanation for Dy_yO_x deposition is modification of the double layer, and increase in adsorption of Dy^{3+} and therefore the ions see a much larger potential above the magnets due to the Frumkin, or double layer correction (see §1.4.5). This hypothesis will be explored with a model system in the next chapter.

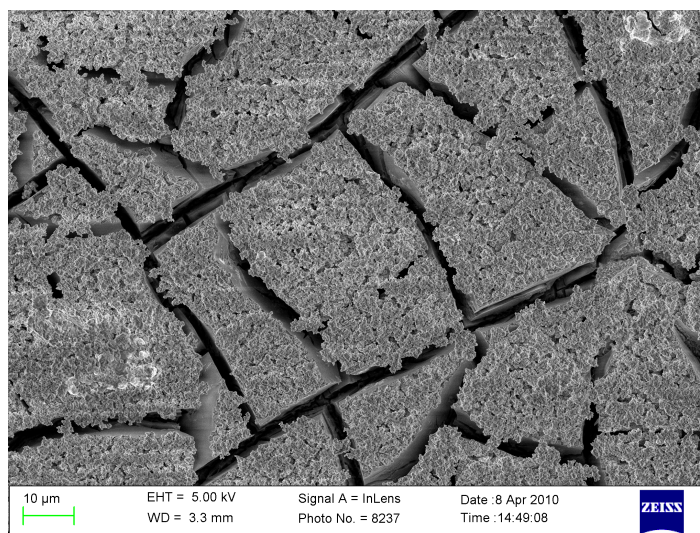


Figure 4.40: SEM micrograph of a Dy_yO_x deposit.

4. ELECTRODEPOSITION ABOVE PERMANENT MAGNET ARRAYS

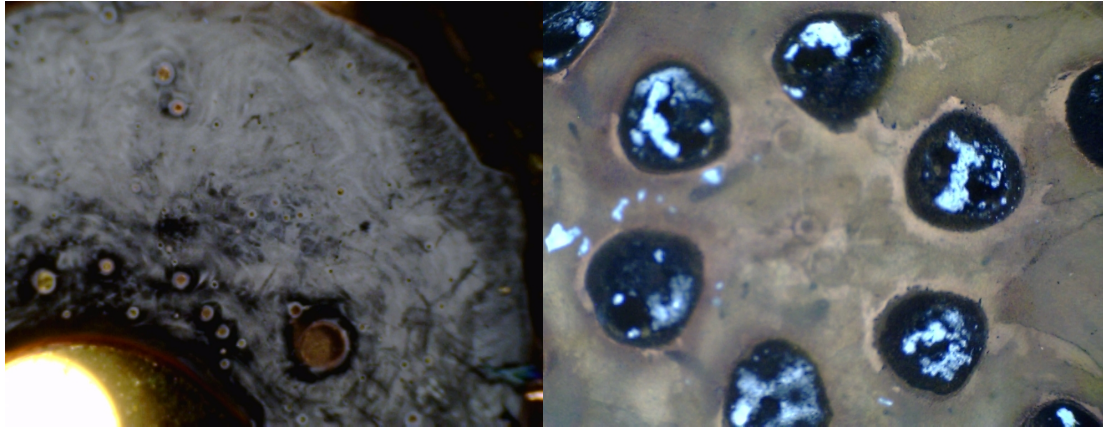


Figure 4.41: Optical micrographs of DyO_x above (a) 13 mm OD 5 mm ID ring magnet on 25 nm Au/Ru/Si wafer, and (b) hexagonal aligned array on a $50\mu\text{m}$ Ag foil. The grey/white deposits are Dy_yO_x , the black deposits are thick Cu_yO_x , and the lighter pink-brown in Cu meta.

Table 4.9: EDX elemental analysis of DyO_x deposits from the 3.3mM $\text{Dy}(\text{NO}_3)_3$ solution above a 13 mm OD 5 mm ID ring magnet.

		1	2	3
Element	Edge	Atomic %	Atomic %	Atomic %
C	K	7.8	7.4	5.2
O	K	76.7	76.5	61.2
S	K	3.7	3.6	2.4
Cu	K	2.7	2.9	7.8
Dy	L	9.0	9.6	23.4
Au	L	0.1	0.1	0.1
Total		100	100	100

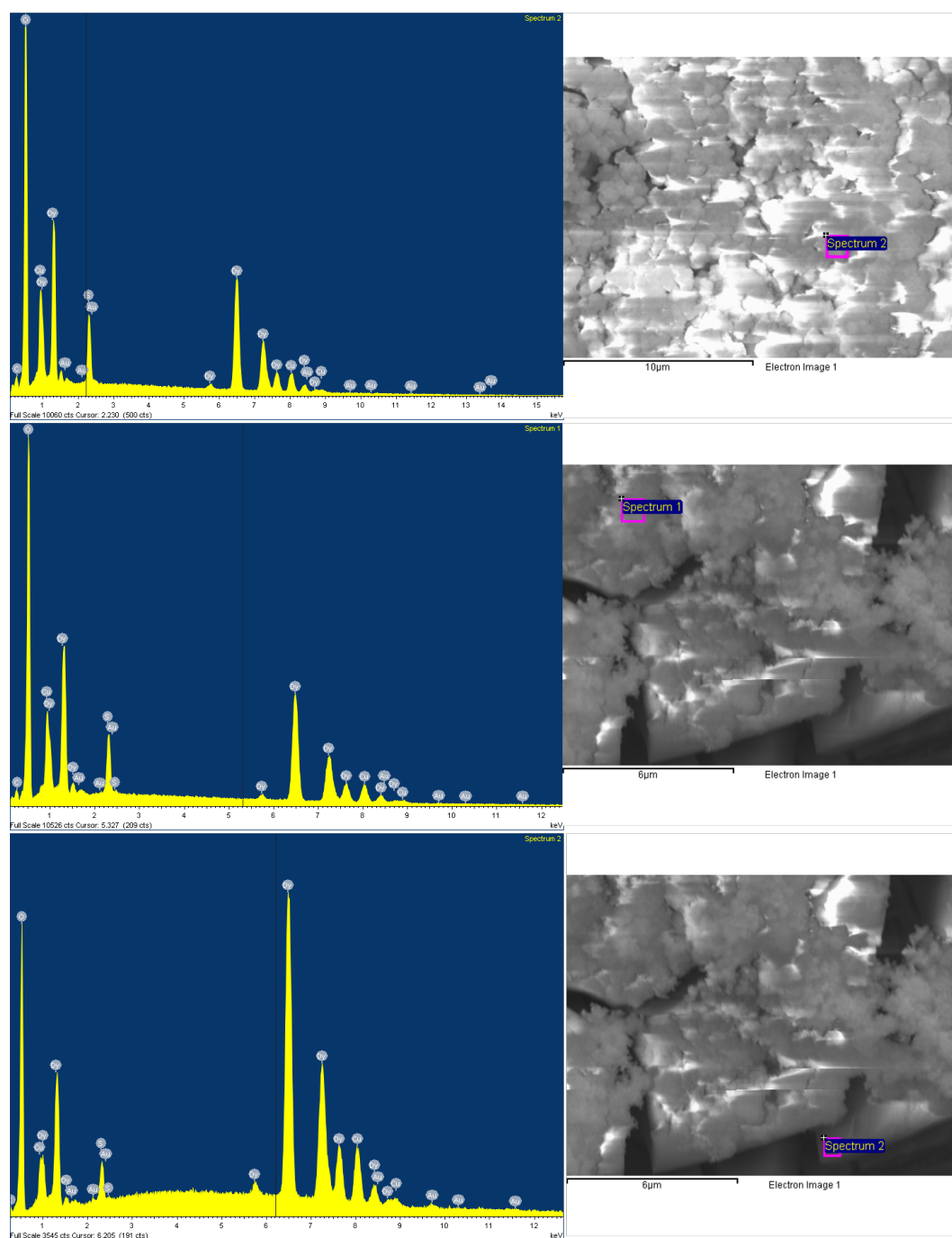


Figure 4.42: EDX analysis of DyO_x deposits above a 13mm ID 5 mm OD ring magnet, panels on the left are EDX spectra, panels on the right are SEM micrographs indicating the regions scanned in the EDX spectra.

4. ELECTRODEPOSITION ABOVE PERMANENT MAGNET ARRAYS

4.5 Scalability

The same Co solution ($2\text{ M CoSO}_4 + 0.6\text{ M H}_3\text{BO}_3$, and $1\text{ M CuSO}_4 + 1.2\text{ M H}_2\text{SO}_4 + 0.25\text{ mM KCl}$) was used as before. $\text{Co}_{80}\text{Fe}_{20}$ arrays of $85\mu\text{m} \times 85\mu\text{m}$ squares 25 nm thick, on top of Ru seeded Si wafers, and capped with 100 nm Cu were used as magnetic templates. Deposition was carried out under an externally applied 1.5 T field in order to magnetise the CoFe arrays. Well defined Cu arrays were observed; conforming to the CoFe arrays buried in the Cu capping layer.

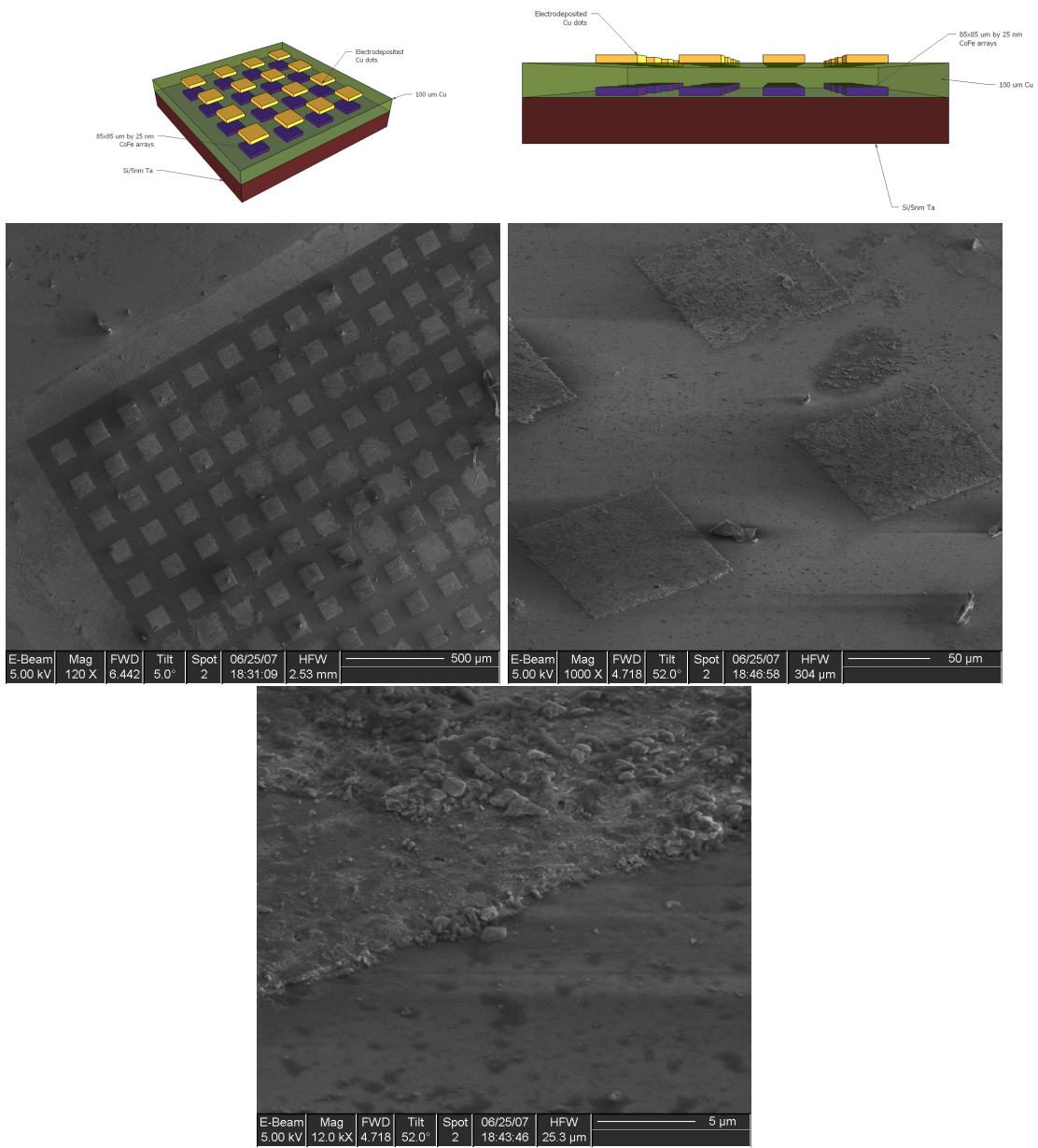


Figure 4.43: Cu micro array deposits: (a) elevation, and (b) isometric projection of working electrode used; (c-e) SEM micrographs of Cu microarray deposits.

4.6 Conclusions

In the bulk solution, diffusion prevents the magnetic field gradient force from concentrating/separating any species. Therefore any effects we see must be occurring inside the diffusion layer, or even in the double layer. In the case of copper deposition, any influence must be on the Cu^{2+} (paramagnetic) to Cu^+ (diamagnetic) step and hence before the ion has become an adatom on the surface. To deposit on the cathode surface, the ions must travel into the double layer, leading to a large concentration of metal ions close to the surface (see §1.4). This suggests that it is the susceptibility of the metal ions near the electrode that is important not the bulk susceptibility of the solution. This conclusion is supported by observation of the deposit patterns for all three bulk susceptibility cases ($\chi > 0$, $\chi \approx 0$, and $\chi < 0$) which were seen to follow the pattern of $|\mathbf{B}|$.

Magnetic templating is possible using permanent magnet arrays since paramagnetic ions tend to deposit in regions of large magnetic field. Inverse patterns are not directly possible as no effect on surface morphology was observed for diamagnetic ions. However, by using concentrated rare-earth paramagnetic solutions inverse patterns can be deposited with the metal ions of interest. Preliminary studies at micron dimensions suggest that magnetic focusing can be scaled down to patterns useful in micro- or nano-electronics.

Dysprosium oxides were deposited in high magnetic field regions using the balanced susceptibility solution; opening up a new avenue of study in the electrodeposition of rare earth metals, and are explained by the increased adsorption of Dy^{3+} ions in high field regions. It remains to be seen whether the dysprosium is deposited as a metal, and if it is a stable process.

However a number of questions or issues still remain: (i) Why do the patterns follow contours of $|\mathbf{B}|$ rather than ∇B or ∇B^2 ? (ii) Is the origin of the effect from modification of the double layer, ion adsorption, or even a magnetic field effect on the kinetics of the system? (iii) Does the constant change in surface area significantly alter the local current densities, thereby invalidating any conclusions drawn from total current measurements? To clarify the influence of the applied magnetic field a model liquid-liquid phase electrochemical system needs to be studied. The benefit of this approach is that it separates the effects on the kinetic, diffusion and convective properties of an electrochemical system in a predictable manner, without altering the electrode surface. The results and implications of such a model system will be presented in the next chapter.

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Chapter 5

Magnetoelectrochemistry with Model Systems

5.1 Introduction

Re-examining the structure of the metal, solution interface, we defined two distinct regions; the diffusion layer and the double layer. We saw that the diffusion layer is typically 1 – 10 μm thick, and ion motion is driven by diffusion. In contrast the double layer is a highly compact region much closer to the electrode surface, on the order of 0.5 – 10 nm, with all ion motion dominated by the strong electrostatic fields in the compact double layer, coupled with a diffuse layer. The diffusion layer can be influenced by convection, forced or natural, while the double layer is sensitive to surface tension, and excess charge distributions. To date all measured magnetic effects have been due to the Lorentz force and field gradient force on the diffusion layer, as argued in chapter 2; and in chapter 3 we examined further evidence for Lorentz force effects in Cu deposition and metal corrosion. There have been no reports of any effects on the double layer.

Following the puzzling results of the dot array morphologies in chapter 4, a model system is required to study the interaction of an electrochemical system and a magnetic field; capturing the essence of the system in a consistent phenomenological model. To further this end, the nitrobenzene redox system in acetonitrile was chosen as the primary model system. The rationale for this are manifold. Nitrobenzene itself is a commonly used solvent, and the electrochemical system remains liquid-liquid, simplifying matters as the effective surface area does not change to during an experiment unlike metal deposition or corrosion as is commonly used in most magneto-electrochemical experiments. Nitrobenzene is known to be an outer sphere reversible one electron transfer system [1], which forms a stable radical anion in aprotic media upon reduction.



The reduced species $\text{NB}^{\bullet-}$ is relatively long lived in aprotic polar solvents such as acetonitrile [1]; and as well as being paramagnetic, it also has an unusually large kerr coefficient [2]; and is a well known system which has been used to characterise the performance of ionic liquids [3]. Minimisation of electro-migration effects were also important in the selection of active species, and the reactant, NB, is neutral in solution. This allows larger concentrations of NB to be used without seeing migratory mass transport. If the valence of the ions and the concentration of the ions were higher, then direct interactions between the particles would become more important, especially in the double layer.

It is important to understand the system we wish to characterise, and distinguish between the diffusion layer and double layer, and to carry out comparison experiments in different systems. Thus this chapter is divided into four parts, the first is dedicated to the electrochemical properties of the model system in question, the second concentrates on the influence of the Lorentz force on the diffusion layer, the third part on the response of the double layer, and finally the fourth consists of two comparison systems (ferrocene and anthracene).

5.2 Nitrobenzene

5.2.1 Electrochemical System

Before studying the effects of external magnetic fields on the electrochemical processes it is important to have a clear understanding of the basic phenomena in zero field. To this end DC, sweep, pulse and AC techniques were used to characterise the reduction of nitrobenzene (NB) at room temperature. Solutions consisted of 0.1 mol l^{-1} NB, and either 0.2 or 0.5 mol l^{-1} tetrabutylammonium perchlorate (TBAP) in acetonitrile, and bubbled with argon prior to use. Three electrode configurations were used, (i) two face to face 0.5 mm diameter Pt millielectrodes parallel to gravity with an Ag/Ag^+ luggin capillary pseudo-reference electrode, (ii) a 0.5 mm diameter Pt disc working electrode parallel to gravity with a Pt mesh counter electrode and a Ag/Ag^+ 0.1 M AgNO_3 Vycor frit reference electrode, and (iii) a 0.5 mm diameter Pt disc working electrode perpendicular to gravity with a Pt mesh counter electrode and a Ag/Ag^+ 0.1 M AgNO_3 Vycor frit reference electrode. All chemicals were used as delivered, and the working electrodes were polished using diamond lapping paper. Measurements were taken with one of three systems, an EG& G PAR 263A potentiostat, a Solartron 1280B, or a CHI 660C workstation.

5.2.1.1 Cyclic Voltammograms

For simple reversible systems of the type $O + n e^- \rightarrow R$ the peak current response to a voltage sweep (linear or cyclic) is

$$i_{p,c} = -2.69 \times 10^5 n^{3/2} A D_0^{1/2} [O]_{\infty} v^{1/2} \quad (5.2)$$

which was discussed in chapter 1. Features of a reversible system include [4]:

- $i_p \propto v^{1/2}$
- E_p independent of v
- $|E_p - E_{p/2}| = 56.6/n \text{ mV}$
- $E_{p,a} - E_{p,c} = 57.0/n \text{ mV}$ ($E_{\lambda} \ll E_{p,c}$ or $E_{\lambda} \gg E_{p,a}$)
- $|i_{p,a}|/|i_{p,c}| = 1$

Not all these observations hold for quasi-reversible or irreversible reactions; E_p is no longer independent of scan rate, the peaks are generally broader and lower and $|I_{p,a}|/|I_{p,c}| \rightarrow 0$ for greater degrees of irreversibility. Cyclic voltammogram characteristic features now appear as: [5]

- $dE_p/d \log v = 29.6 \text{ mV}/(\alpha n')$
- $|E_p - E_{p/2}| = 47.7 \text{ mV}/(\alpha n')$

Solvent	Bp	Fp	Vapour Pressure	Density	Viscosity	Conductivity $\times 10^{-9}$	Relative Permittivity	Dipole Moment
	C	C	mmHg	g cm^{-3}	cP	S cm^{-1}		D
Water	100	0	23.8	0.997	0.89	60	78.39	1.85
Methanol	64.5	-97.7	127	0.7864	0.551	1.5	32.7	2.87
Ethanol	78.3	-114.5	59	0.7849	1.083	1.4	24.6	1.66
Acetone	56.1	-94.7	231	0.7844	0.303	5.0	20.6	2.7
Acetonitrile	81.6	-43.8	88.8	0.7765	0.341	0.6	35.9	3.53
Dimethyl Sulfoxide	189	18.5	0.6	1.095	1.99	2.0	46.5	4.05
Nitrobenzene	210.8	5.76	0.28	1.1983	1.62	0.2	34.8	4

Table 5.1: Properties of some common solvents

Solvent	ϵ_s	ϵ_{op}	ϵ_{inf}	$\epsilon_{op}^{-1} - \epsilon_s^{-1}$	τ_d (ps)	τ_l (ps)
ACN	37.5	1.8	2	0.528	3.3	0.2
NB	35.7	2.4	4.1	0.389	45.6	5.2

Table 5.2: Dielectric properties of acetonitrile and nitrobenzene

5. MAGNETOELECTROCHEMISTRY WITH MODEL SYSTEMS

with the peak current described thus:

$$i_{p,c} = -2.69 \times 10^5 n(\alpha n')^{1/2} A D_0^{1/2} [O]_{\infty} v^{1/2} \quad (5.3)$$

In both the reversible and irreversible case $i_p \propto v^{1/2}$, so to distinguish a quasi-reversible and reversible reaction both treatments are used. From figures 5.2 and 5.3 it is possible to extract the diffusion coefficient and charge transfer coefficient for (a) the reversible case, and (b) the irreversible case (see table 5.4).

Table 5.3: Fitting results from Randles-Sevcik Plots

	Reversible “ n ”	D $10^{-5} \text{ cm}^2 \text{ s}^{-1}$	Irreversible α	D $10^{-5} \text{ cm}^2 \text{ s}^{-1}$
Reduction	0.66	2.25	0.62	2.64
Oxidation	0.66	2.31	0.62	2.70

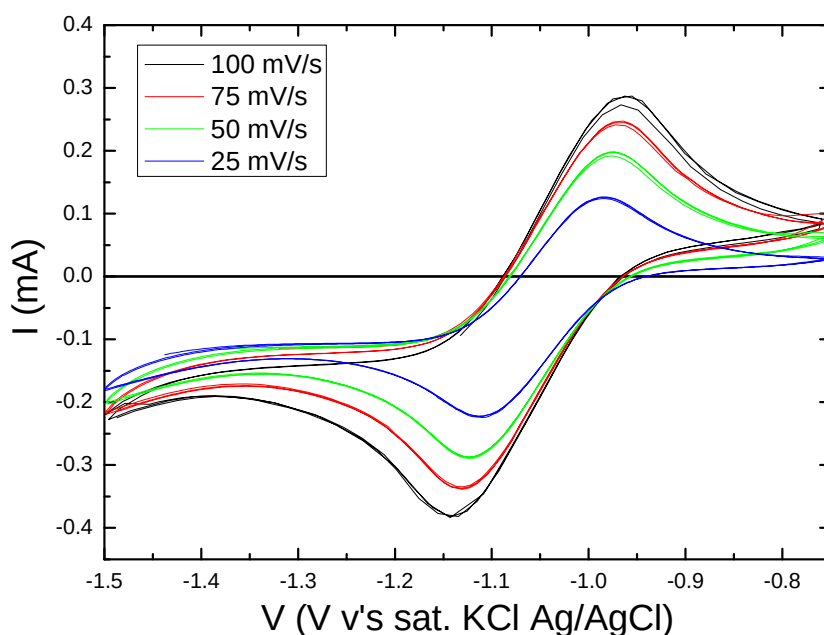


Figure 5.1: Cyclic voltammograms of 0.1 M Nitrobenzene in 0.5 M TBAP/ACN. The peak shifts indicated the quasi-reversibility of the system.

Using a reversible treatment we derive an effective electron transfer of 0.66, which we know is not the case for NB. Using the more correct irreversible approach, we see that in fact it is the electron transfer coefficient, $\alpha_c = 0.66$, which gives an apparent $n < 1$. An electron transfer coefficient $\neq 0.5$ informs us that the energy barrier between reduction and oxidation is not symmetric, that $\text{NB}^{\bullet-}$ is less stable in solution, and that the neutral species is more likely to be found in solution. Further evidence for an

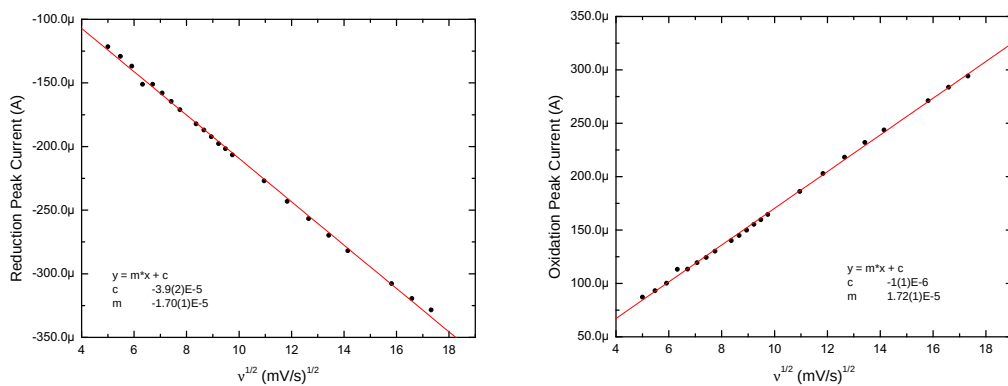


Figure 5.2: Randles-Sevcik reduction and oxidation plots of NB

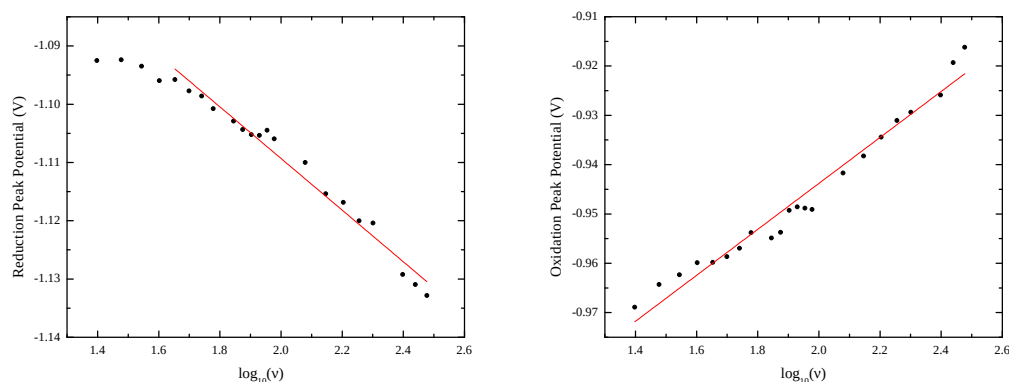


Figure 5.3: The dependence of peak potential on $\log(v)$ for (a) reduction and (b) oxidation of NB/NB $^{\bullet-}$

irreversible or quasi-reversible system comes from the diffusion coefficients, and the peak spacings. The larger extracted oxidation diffusion coefficients are attributed to an irreversible chemical step removing NB $^{\bullet-}$ from the electrode surface, and the peak separation is observed to increase with scan rate. To illustrate this, the peak current ratios $|I_{p,a}|/|I_{p,c}|$ and the charge transfer coefficient α_c are plotted versus the square root of the scan rate $v^{1/2}$ (fig. 5.4).

A homogeneous chemical reaction takes place after reduction, protonating the NB $^{\bullet-}$ radical followed by regeneration of NB via



At shorter time scales, i.e. faster sweep rates there is not enough time for the chemical step to decrease the concentration of NB $^{\bullet-}$ at the electrode, thus the ratio of the oxidation peak current to the reduction peak current increases towards 1 (fig. 5.4). It is still possible to treat the system reversibly but care is needed in the calculation of kinetic parameters from cyclic voltammograms. At low levels of water contamination

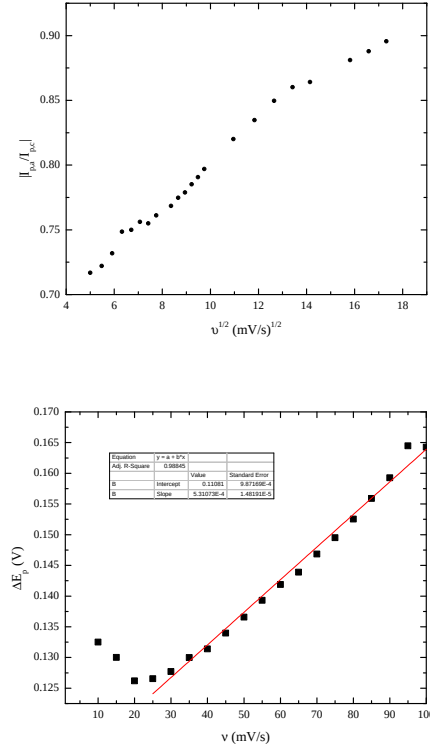


Figure 5.4: (a) The ratio $|I_{p,a}|/|I_{p,c}|$ and (b) ΔE_P versus v

the protonation can initially stabilise the reduced form $\text{NB}^{\bullet-}$. The degree of ion pairing influences the reversibility/irreversibility of the reduction process, and thermodynamically it will shift the standard potential in the positive direction

$$E^0 = E_{NB}^0 + \frac{RT}{nF} \ln(1 + K_a[Z]) \quad (5.5)$$

where E_{NB}^0 is the standard potential for the redox reaction of NB, $[Z]$ is the concentration of the ion pairing agent (H^+ in this case), and K_a is the association constant [6]. On the oxidation side, the reaction follows a predissociation mechanism as long as the extent of protonation is not too great. The energy cost of the predissociation makes the oxidation wave shift towards positive potentials, and as the protonation increases (i.e. higher levels of water contamination) the predissociation increases leading to a gradual disappearance of the oxidation wave. In the absence of protonation, the relative concentrations of NB and $\text{NB}^{\bullet-}$ at the electrode surface at steady state can be described by

$$\frac{(c_{\text{NB}})_{x=0}}{c_{\infty}} = 1 - \frac{i}{i_L}, \quad \frac{(c_{\text{NB}^{\bullet-}})_{x=0}}{c_{\infty}} = \frac{i}{i_L} \quad (5.6)$$

where $i_L = nFAc_{\infty}D/\delta$ is the mass transport limited current at steady state (see §1.5), $(c_{\text{NB}})_{x=0}$ and $c_{\text{NB}^{\bullet-}}$ are the NB and $\text{NB}^{\bullet-}$ concentrations at the electrode surface, and c_{∞} is the bulk concentration of NB. With protonation these relations become

$$\frac{(c_{\text{NB}})_{x=0}}{c_{\infty}} = 1 - \frac{i}{i_L}, \quad \frac{(c_{\text{NB}^{\bullet-}})_{x=0} + (c_{\text{NBH}^{\bullet}})_{x=0}}{c_{\infty}} = \frac{i}{i_L} \quad (5.7)$$

At equilibrium the protonation reaction behaves as

$$(c_{\text{NB}^{\bullet-}})_{x=0} = \frac{(c_{\text{NB}^{\bullet-}})_{x=0} + (c_{\text{NBH}^{\bullet}})_{x=0}}{1 + K_a[Z]} \quad (5.8a)$$

$$= \frac{i}{i_L} \frac{1}{1 + K_a[Z]} c_{\infty} \quad (5.8b)$$

This equation tells us that as the proton concentration or association constant increases, the concentration of $\text{NB}^{\bullet-}$ decreases. Adopting a simplified approach, we treat the protonation as a non-coupled follow up first order reaction described by

$$C_R(t) = C_R^0 e^{-t/\tau} \quad (5.9)$$

where C_R is the $\text{NB}^{\bullet-}$ concentration at the electrode surface, C_R^0 is the $\text{NB}^{\bullet-}$ concentration at the electrode surface at the half-wave potential, before the return sweep, and τ is the decay constant. Likewise we assume that $\tau < t_p$, where t_p is the time taken to sweep the voltage from the half-wave potential to the oxidation peak current.

Recalling that the peak current in cyclic voltammograms for reduction is

$$i_{p,c} = -2.69 \times 10^5 n^{3/2} A D_O^{1/2} [O]_{\infty} v^{1/2} \quad (5.10)$$

and that a similar equation can be written for an oxidation current

$$i_{p,a} = -2.69 \times 10^5 n^{3/2} A D_R^{1/2} [R]_{\infty} v^{1/2} \quad (5.11)$$

where n is the number of electrons transferred, D_O , and D_R are the diffusion coefficients of the oxidised and reduced species, $[O]_{\infty}$ is the bulk reactant concentration, $[R]_{\infty}$ is the bulk product concentration, and v is the voltage scan rate, the ratio of the oxidation current to reduction current is

$$\frac{I_O}{I_R} = \frac{D_R^{1/2} [R]_{\infty}}{D_O^{1/2} [O]_{\infty}} \quad (5.12)$$

For a reversible reaction, $\frac{I_O}{I_R} = 1$, and at the electrode surface $C_R(t_p) D_R^{1/2} = C_O^0 D_O^{1/2}$, therefore we define

$$C_R^0 = C_O^0 \sqrt{\frac{D_O}{D_R}} \quad (5.13)$$

where C_O^0 is the initial concentration of NB at the electrode surface before electrolysis, which is the bulk concentration. The ratio of peak currents then result in the following

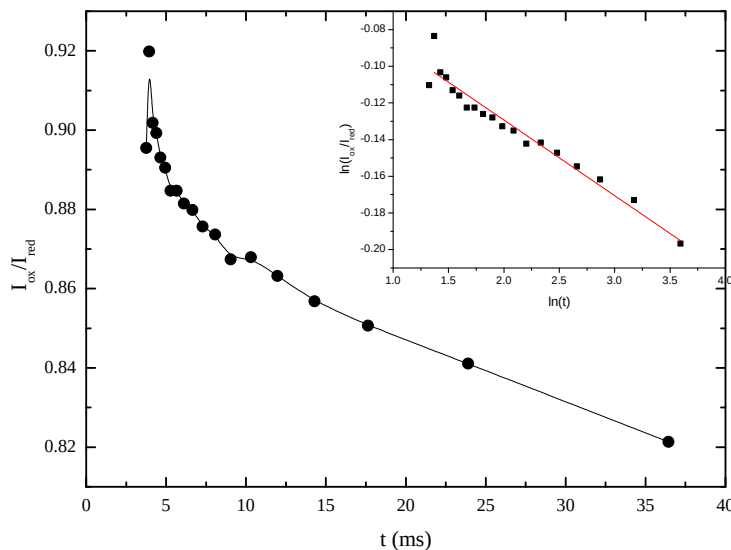


Figure 5.5: The decay of I_O/I_R with time, indicating the existence of a follow up chemical reaction, a black β -spline is included as a guide for the eye. The inset shows a plot of $\ln(I_O/I_R)$ versus $\ln(t)$.

relationship

$$\frac{I_O}{I_R} = \left(\frac{I_O}{I_R} \right)^0 \sqrt{\frac{D_O}{D_R}} e^{-t/\tau} \quad (5.14a)$$

$$\ln\left(\frac{I_O}{I_R}\right) = \ln\left(\frac{C_O^0}{C_R^0} \sqrt{\frac{D_R}{D_O}}\right) - \frac{1}{\tau}t \quad (5.14b)$$

where $\left(\frac{I_O}{I_R}\right)^0$ is the current ratio at $t = 0$.

From figure 5.5 we can see that there is indeed a first order chemical reaction from the decay of I_O/I_R with time, and from the inset we derive the characteristic decay constant, or lifetime $\tau = 24$ ms. The intercept gives a value of $C_O^0 = 0.096 \text{ mol l}^{-1}$, using the measured values of the diffusion coefficients in table 5.4 which agrees with our assumption of $C_O = C_O^0 \sqrt{\frac{D_O}{D_R}}$ which is ≈ 0.099 ; thus showing that our analysis, while not strictly correct give us a good qualitative description.

5.2.1.2 Rotating Disc Electrode

To study the kinetics of the redox reaction, a carbon rotating disc working, with a diameter 3 mm, was used to generate well defined hydrodynamic conditions. Linear sweep voltammograms at 100 mV s^{-1} were carried out at different rotation rates and Koutecky-Levich plots were generated at different potentials (see figs. 5.6 and 5.7). The kinetic current was extracted from the inverse intercept of the curves, and its dependence on applied potential was characterised (fig. 5.7). At E^0 ($\sim -1.29 \text{ V}$) the

kinetic current is -0.9 mA which gives a kinetic constant of $k_0 = 1.3 \cdot 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ on glassy carbon.

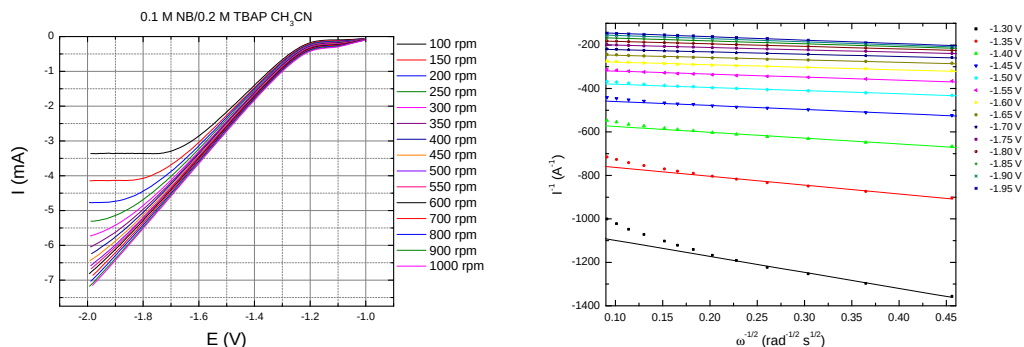


Figure 5.6: (a) Linear sweep voltammetry at a glassy carbon RDE, (b) Levich plots

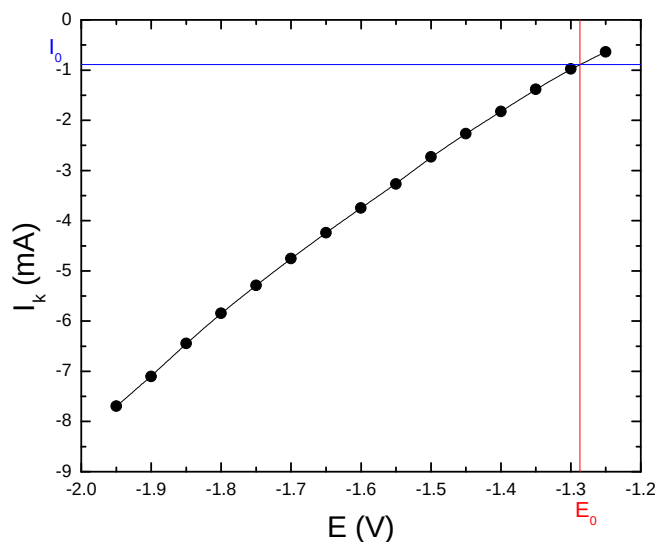


Figure 5.7: Extracted kinetic current as a function of applied voltage using a β -spline interpolation.

5.2.1.3 Pulse measurements

Using chronoamperometry, the diffusion coefficient can also be measured, recalling that the current after a potential step can be described by the Shoup-Szabo equation (see §1.5.1.1)

$$|I(t)| = A + Bt^{-1/2} + 0.2732 A \exp\left(\frac{-0.3911 B\pi^{1/2}}{At^{1/2}}\right) \quad (5.15)$$

where $A = \pi FrncD$ and $B = \pi^{1/2} Fr^2 ncD^{1/2}$ and a simple C program was written to perform the fitting. The exponential term is assumed to be much smaller

than the other two terms and is treated as a perturbation on the linearised system. A linear least squares fit is performed on $|I(t)|$ vs. $t^{-1/2}$ computing the intercept A_1 and the slope B_1 . Next a linear least squares fit is carried out on $|I(t)| - 0.2732A_1 \exp(-0.3911\pi^{1/2}B_1/A_1 t^{1/2})$ vs. $t^{-1/2}$ to calculate the intercept A_2 and slope B_2 . This is repeated until the values stabilise. Rearranging A and B allows one to calculate D and nc thus:

$$D = \frac{A^2 r^2}{B^2 \pi} \quad (5.16)$$

$$nc = \frac{B^2}{Fr^3 A} \quad (5.17)$$

$$(5.18)$$

Calculation of nc , is used to ensure the fitting is reliable.

The diffusion coefficient, D , was found to be $2.49 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, and $nc = 0.095 \text{ mol l}^{-1}$ in agreement with the voltammograms. Thus showing that the assumption of a one electron quasi-reversible system is valid.

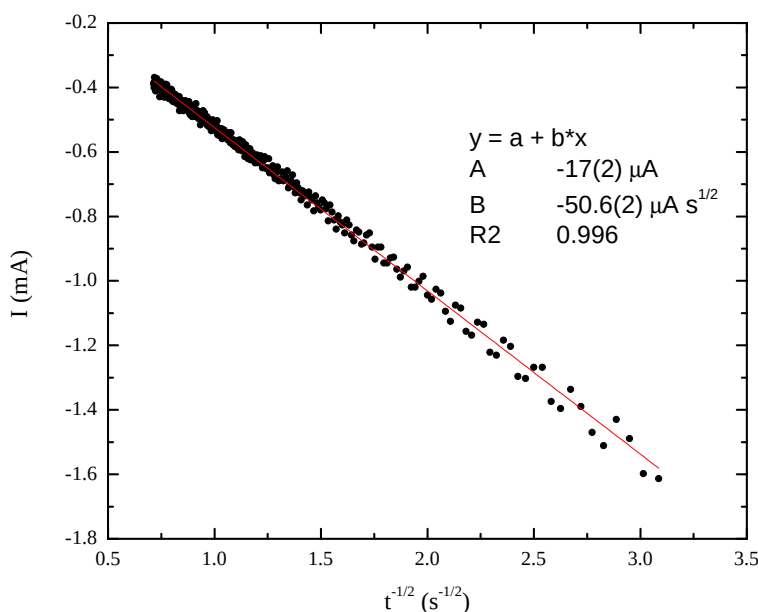


Figure 5.8: Current response of 0.1 M NB to a -1.2 V potential step versus $t^{-1/2}$

Adsorption on the electrode surface can also be studied by applying more complicated pulse methods such as double pulse chronocoulometry discussed in chapter 1. As a reminder, the voltage is stepped into an active reduction regime, and then stepped back to zero after a defined pulse length. The total charge built up at the electrode during the first step Q_F , and the reverse discharge Q_R are related to the pulse length by

$$Q_F(t) = \frac{2nFAD^{1/2}c_\infty}{\pi^{1/2}} t^{1/2} \quad (5.19)$$

and

$$Q_R(\theta) = \frac{2nFAD^{1/2}c_\infty}{\pi^{1/2}}\theta^{1/2}, \quad t < \tau \quad (5.20)$$

where $\theta = \tau^{1/2} - t^{1/2} + (t + \tau)^{1/2}$. From the difference between the intercepts, the charge due to adsorption was $-31.5 \mu\text{C}$, which gives a $\text{NB}^{\bullet-}$ -surface excess of $\Gamma_0 = 40 \text{ nmol cm}^{-2}$.

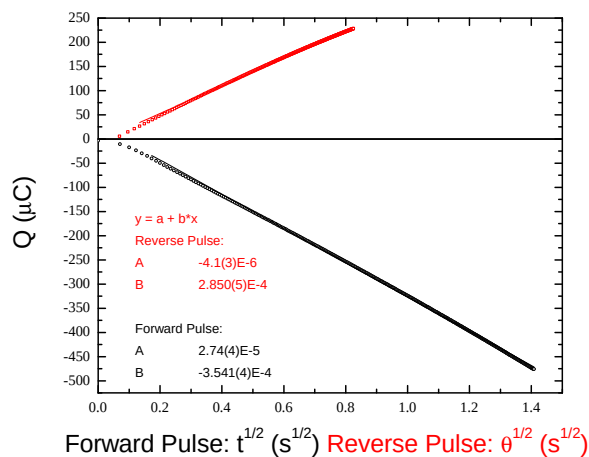


Figure 5.9: Double pulse chronocoulometry: (a) Voltage pulse and current and charge responses, Q_F and Q_R are the forward and reverse pulse charges, (b) a plot of $Q_F(t^{1/2})$ and $Q_R(\theta)$ for the reduction of 0.1 M nitrobenzene in 0.5 M TBAP/ACN. The non-linearity at short times is due to the response of the potentiostat.

5.2.1.4 Impedance Spectroscopy

Following this, impedance spectroscopy was used to measure the kinetic and mass transport properties of NB. Figure 5.10.b shows a typical Nyquist plot for the reduction of NB at the reduction peak potential seen in figure 5.10.a. The real and imaginary components of the measured impedance were simultaneously fitted, using a Randles circuit (see fig. 5.11). The circuit was assumed to consist of the charge transfer resistance in series with a generalised finite Warburg diffusion resistance, both in parallel to the double layer capacitance and all then in series with the solution resistance, which includes the uncompensated iR drop on the reference electrode. All fits were checked for linearity using the Kramers-Kronig transformations.

Table 5.4: Fitting results from complex-plane fit

R_s	R_{ct}	C_{dl}	W_r
Ω	Ω	nF	k Ω
65	73	26	4.5

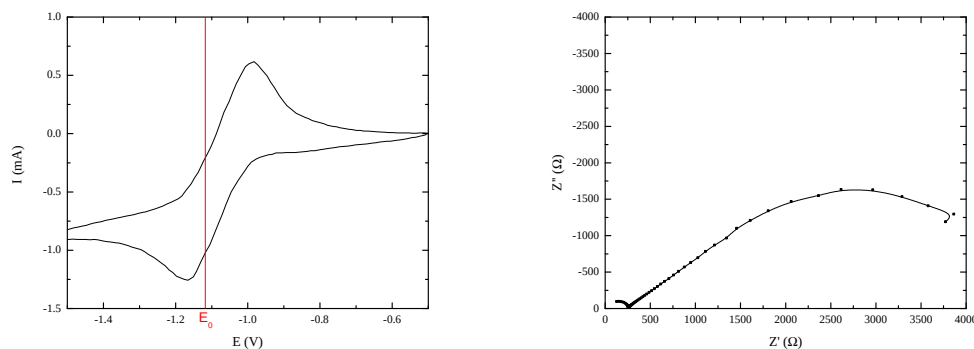


Figure 5.10: (a) Cyclic voltammogram of 0.1 M NB and (b) Impedance spectrum at the standard potential shown in (a).

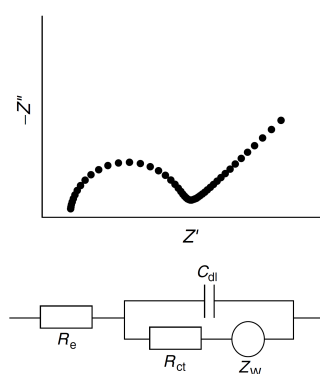


Figure 5.11: Equivalent circuit used to fit impedance spectra

The kinetic constant k_0 was measured to be $= 2.0 \cdot 10^{-3} \text{ cm s}^{-1}$ at E^0 (fig. 5.10); agreeing favourable with the RDE measurement in figure 5.7. However it is important to note that the impedance measurements were carried out at a Pt electrode compared to a glassy C electrode during RDE measurements. The diffusion coefficient, calculated from the Warburg resistance also agrees well with previous data, and is measured to be $2.3 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

Two methods were used to measure the double layer capacitance and charge transfer resistance as a function of applied potential. The first involved measuring a full impedance spectroscopy frequency sweep at a range of potentials, and carrying out fits to the data (see fig. 5.13.a). The second involved measuring the cell impedance at a fixed frequency while applying a potential sweep (see fig. 5.14). Since we are only interested in the properties of the double layer and charge transfer kinetics the frequency used was 10 kHz. Inspecting figure 5.12, a typical Nyquist plot at the reduction potential, we can see that 10 kHz is close to the semicircle maximum, corresponding to the impedance of R_{ct} and C_{dl} in parallel. To see any contributions by the Warburg impedance, frequencies lower than 200 Hz are needed, and for a reliable signal to noise ratio, frequencies less than 50 Hz are preferred in this system (fig. 5.12). To simplify the model further, iR compensation was used to eliminate the solution resistance re-

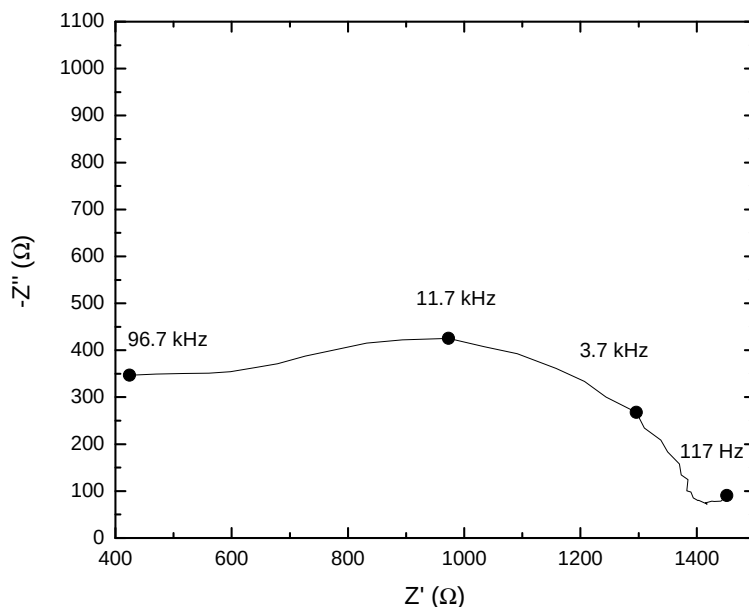


Figure 5.12: Typical high frequency impedance spectrum during the reduction of NB

ducing the model to a two component system of R_{ct} and C_{dl} in parallel. R_{ct} and C_{dl} can be determined explicitly from one frequency by

$$C = \frac{Z''}{\omega^2(Z''^2 + Z'^2)}, \quad \text{and} \quad R = \frac{Z''^2 + Z'^2}{Z'} \quad (5.21)$$

resulting in a curve such as in figure 5.14.a. In both methods the point of zero charge (pzc) is clearly visible, corresponding to the capacitance of the diffuse double layer, and the larger wings correspond to the capacitance of the Helmholtz layer. It is interesting to note that a secondary pzc is observed in the C-V curve obtained by full fitting of the data which does not appear in the fixed frequency measurement. The origin of this is most likely the supporting electrolyte and solvent. The main peak is due to the pseudo-capacitance of the reduced species $\text{NB}^{\bullet-}$ which can only appear on the negative side of E^0 ; the neutral species will make no measurable contribution to the double layer capacitance as it is dependent on excess charges. The dependence of the charge transfer resistance is mapped out in figures 5.13.b and 5.14.b, and we can see that the resistance goes through a minimum at the pzc following the trace of the capacitance. The point of zero charge is the potential at which there is no excess charge on the electrode, and can be seen by integrating the capacitance-voltage curve. (for examples see fig. 5.40)

The current voltage curves can be fitted with a three element Grahame model, consisting of the compact layer capacitance in series with the diffuse layer capacitance of the supporting electrolyte and solvent, and a pseudo-capacitance due to the adsorption of

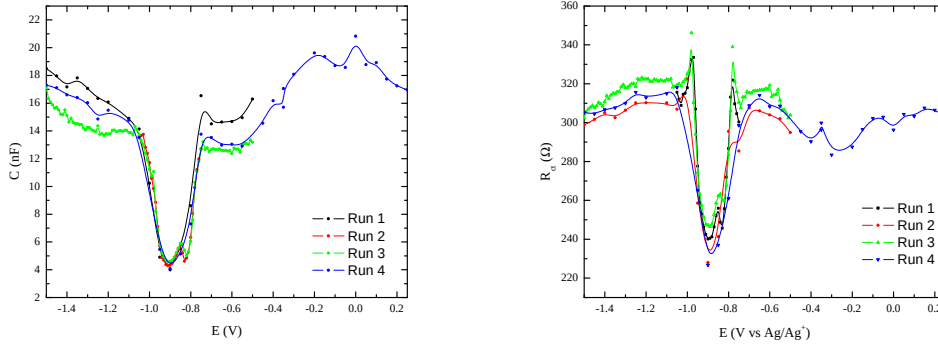


Figure 5.13: Potential dependence of (a) Double layer capacitance of 0.1 M NB solution and (b) charge transfer resistance, from fits of full impedance spectra. Note β -splines are included as guides to the eye, see fig. 5.15 for a model fit.

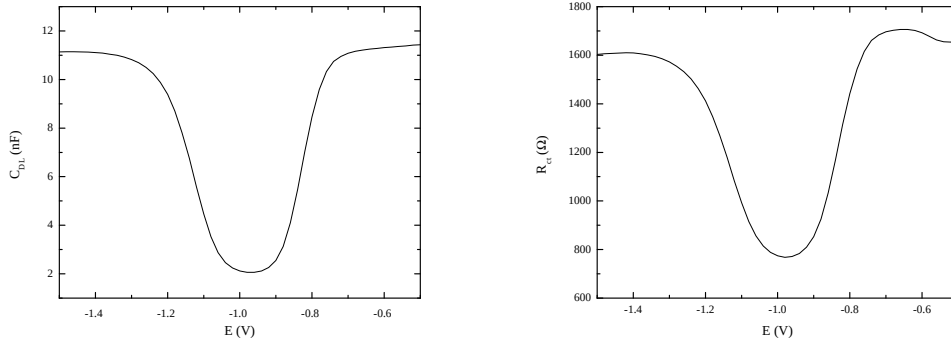


Figure 5.14: Potential dependence of (a) Double layer capacitance of 0.1 M NB solution and (b) charge transfer resistance, using the fixed frequency method.

$\text{NB}^{\bullet-}$, which can only occur for potentials more negative than E^0 .

$$C = \left[\frac{d}{\epsilon_r \epsilon_0 A} + \left[\left(\frac{2e\epsilon_r \epsilon_0 c_1 N_A}{k_b T} \right)^{1/2} \cosh \left(N_1 \frac{ze(\phi_0 - \phi_1)}{2k_b T} \right) \right]^{-1} \right]^{-1} \quad (5.22a)$$

$$+ \left[\left(\frac{2e\epsilon_r \epsilon_0 c_2 N_A}{k_b T} \right)^{1/2} \cosh \left(N_2 \frac{ze(\phi_0 - \phi_2)}{2k_b T} \right) \right]^{-1} + k_{ad} \phi \quad (5.22b)$$

where d is the compact layer thickness, ϵ_r is the relative permittivity, ϵ_0 the permittivity of free space, A is the electrode area, e the elementary charge, c_1 is the concentration of TBA^+ in the diffuse layer, c_2 is the concentration of $\text{NB}^{\bullet-}$ in the diffuse layer, N_A Avogadro's number, k_b is Boltzmann's constant, T is the temperature, z is the ion charge, ϕ_0 is the electrode potential, ϕ_1 and ϕ_2 are the potentials of zero charge, k_{ad} is a specific adsorption coupling constant, and N_1 and N_2 are ideality factors. The first term is the geometric, or compact Helmholtz capacitance, the second is the diffuse double layer capacitance of the supporting electrolyte and solvent, the third term is

the pseudo-capacitance of the adsorbed reduced species $\text{NB}^{\bullet-}$, and the fourth term considers the interaction of non-specific adsorption to electrode potential. A number of simplifications and assumptions were made in the application of this model, firstly in the diffuse double layer, the peak width includes an ideality factor N_1 , N_2 . This is because two important interactions cannot be modelled or measured in this system. In the Stern model (the diffuse layer), the number density of ions near the electrode was modelled by a simple Boltzmann distribution

$$n_i = n_i^0 \exp \left[-\frac{z_i e \phi_\Delta}{k_b T} \right] \quad (5.23)$$

where n_i is the number density of ions, n_i^0 is the number density at the electrode, ϕ_Δ is the potential in the diffuse layer. This ignores any recombination currents in the diffuse layer, which can arise for NB either from the back reaction (oxidation) step, or protonation. This can be written as

$$i = zFAk_r[n_i - n_i^0] \quad (5.24)$$

where k_r is the recombination current coefficient. A recombination current will cause the line width of the capacitance peak to narrow, signified by an ideality factor less than 1, and at maximum recombination the ideality factor becomes 0.5. Another factor not modelled directly is the surface roughness. If there are surface roughness features on the same scale as the diffuse layer thickness, then there will be a distribution of potential. This is a function of position at the electrode surface, described by a roughness function $\tilde{R}$; thereby leading to a broadening of the diffuse layer capacitance as a function of voltage [7]. For a polycrystalline metal surface, the measured pzc is a global average, individual faces can have an excess charge, and this too broadens the diffuse layer C-V peak. Accounting for this surface roughness in a systematic way is beyond the scope of this study, nor is it required, since it is the global values of capacitance we are interested in. Likewise to account for the recombination current, detailed temperature dependent measurements would need to be carried out, possibly beyond the working temperatures of the solvent and solute.

In summary, recombination currents will lead to an ideality factor $N_i < 1$, while surface roughness will broaden it ($N_i > 1$). Another important simplification employed is a discrete pseudo-capacitance E_{pzc} . This is not strictly correct as this diffuse capacitance gradually forms as the voltage sweeps negative, until the reduction potential is reached. This leads to an overestimation of the diffuse layer capacitance close to pzc as shown in figure 5.15.a. Finally, the coupling of adsorption to the electrode potential was assumed to be linear in the measured region, which has been seen in other systems [8].

Table 5.5 shows the fitted parameters to a C-V scan at 10kHz. A Helmholtz capacitance of 11 nF implies that the relative permittivity in this compact layer is ~ 3.5 , given that the Stokes radius for acetonitrile and nitrobenzene are 0.36 nm and 0.55 nm respectively

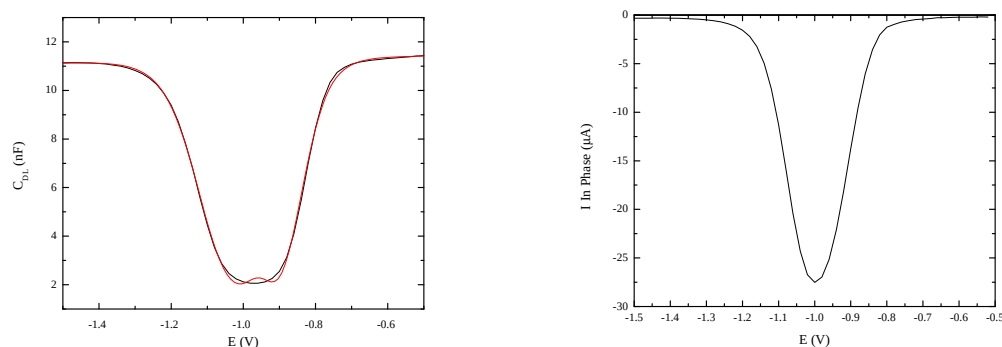


Figure 5.15: (a) Three capacitor series fit to C-V curve of 0.1 M NB at 10kHz, and (b) an in Phase AC voltammogram at 100 Hz, showing the standard potential $E^0 = -1$ V

Table 5.5: Fitting results from three capacitor model for 0.1 M at 10kHz

C_H nF	c_1 $\mu\text{mol l}^{-1}$	N_1	ϕ_1 V	c_2 $\mu\text{mol l}^{-1}$	N_2	ϕ_2 V	k_{ad} nFV
11	197	1.4	-0.93	135	0.8	-1.06	0.56

[9]. This is a common result due to the electrostriction breaking the structure of the solution. The effective pressure on the molecules in the compact layer is in the region of gigapascals [10], aligning all the molecular dipoles and thus lowering the relative permittivity [4, 7, 8]. The concentration of $\text{NB}^{\bullet-}$ in the diffuse layer was found to be much less than the concentration of the neutral species in bulk; $135 \mu\text{mol l}^{-1}$ compared to 0.1 mol l^{-1} , and the point of zero charge ϕ_2 is slightly more negative than E^0 for this potential scale of -1.0 V (see fig. 5.15.b) supporting the conclusion that it is due to a pseudo-capacitance that only occurs when NB is reduced at the electrode surface. As we already observed in §5.2.1 an irreversible chemical reaction (protonation) occurs in solution decreasing the concentration of $\text{NB}^{\bullet-}$ at the electrode surface; manifesting itself as an ideality factor < 1 agreeing with the fitted value of $N_2 = 0.8$. It is not possible to distinguish any surface roughness broadening as it is hidden by the recombination current narrowing. The opposite is true for the supporting electrolyte. An ideality factor > 1 is observed, suggesting that the surface roughness dominates the ideality factor, and little or no recombination current can be expected as TBA^+ is not reactive in this potential window [1].

5.2.2 Lorentz force effects - Whole cell convection

All magnetic field experiments were carried out either in a 1.5 T electromagnet, or 5 T superconducting magnet (both characterised in chapter 3), with the electrodes parallel and perpendicular to the magnetic field, using the methods described in §5.2.1, and the magnets used in chapter 3.

5.2.2.1 Voltammetry

Previously we have discussed the effect of the Lorentz force on the mass transport of the system through forced convection at the electrode surface. To probe the Lorentz force effects on the mass transport properties of the NB redox reaction over a range of applied potential, cyclic and steady-state voltammetry were used. In cyclic voltammetry the mass-transport limited and kinetic regimes are detectable, provided that convection is not too great it is possible to detect the peak currents at various scan rates and construct Randles-Sevcick plots describing the mass transport of the system.

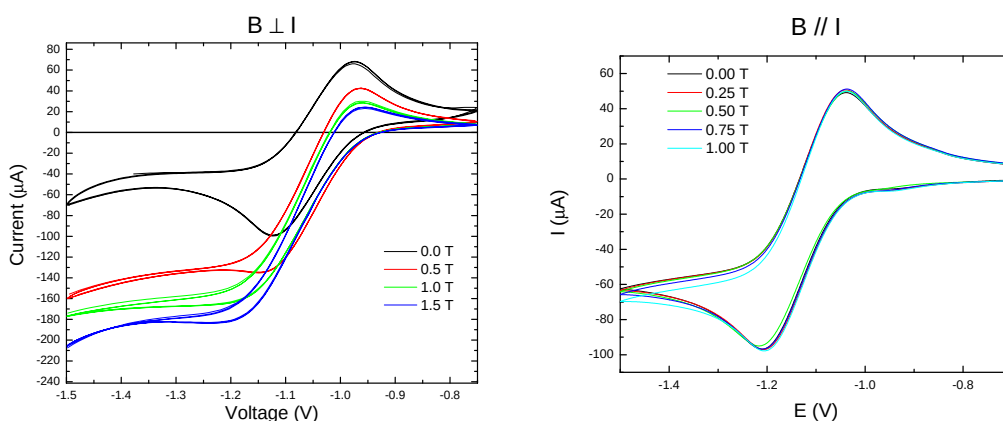


Figure 5.16: Cyclic voltammograms under external magnetic fields (a) perpendicular to current and (b) parallel to current.

Figure 5.16 shows the magnetic field effect for two orientations, (a) the field applied perpendicular to the nominal current, and (b) the field applied parallel to the nominal current. The nominal current direction is defined as the normal to the electrode surface. Concentrating first on the perpendicular alignment, figure 5.17 shows Randles-Sevcick plots for reduction and oxidation of nitrobenzene, and in both cases at all sweep rates the peak currents are enhanced. For the reduction current, at 1.5 T the peak current is almost independent of sweep rate, indicating that the reaction is no longer mass transport limited. Since the supporting electrolyte concentration is large, and migratory effects are weak we know the source of this effect cannot be a modification of the conductivity of the solution, or the diffusion coefficient of NB. Likewise the magnetic field effect on the kinetics is negligible, leaving only a convective effect due to

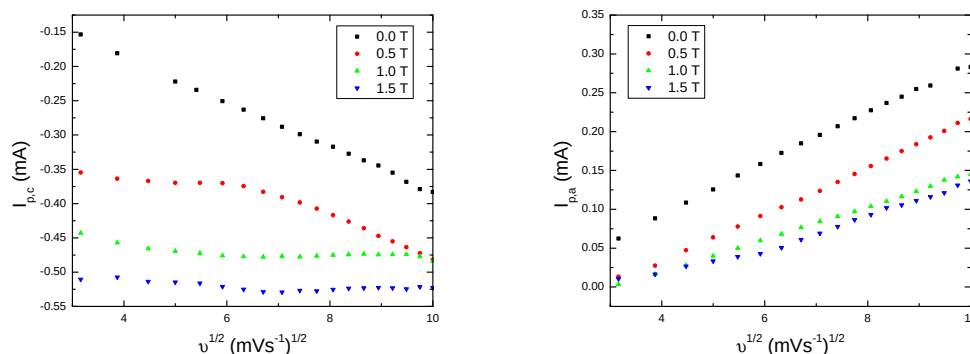


Figure 5.17: Randles-Sevcik plots for (a) reduction and (b) oxidation peak currents under increasing applied perpendicular magnetic fields.

the Lorentz force. The current enhancement as a function of applied field is greatest at slow scan rates (see figs 5.18.a 5.18.b). At slower scan rates the diffusion layer has a longer time to grow, and the Lorentz force stirring is greatest in this region. Once steady-state is reached, the field effect is at its greatest with a power law dependence of $B^{1/2}$, as predicted by Aogaki [11] (figs 5.19).

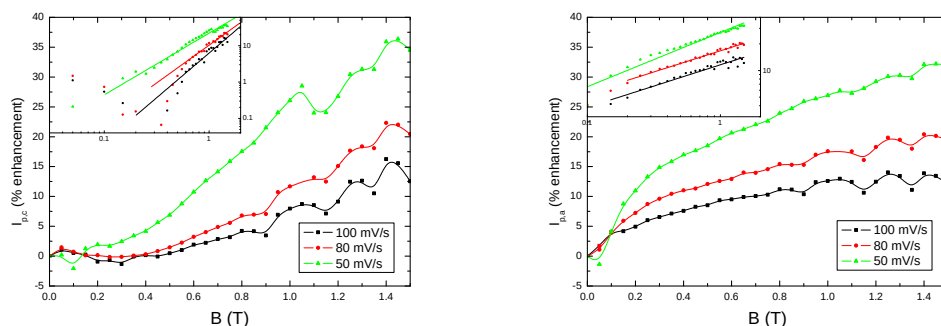


Figure 5.18: Peak current enhancement as a function of applied field for (a) reduction and (b) oxidation; β -splines are guides for the eye, and insets are log-log plots.

So far we have suggested that the Lorentz force is responsible for the current enhancement, if this is true it would be borne out by an angular dependence between B and I , with zero effect for B parallel to I . This is indeed the case as shown back in figure 5.16.b, with almost zero effect on the cyclic voltammograms. Plotting the reduction and oxidation peak currents with the square root of the scan rate, we can see that there is almost no effect on the peak currents for a 1.5 T field parallel to I (fig. 5.20). The peak current enhancements as a function of field for $v = 100 \text{ mV s}^{-1}$ also share the same characteristics, with only a small effect for B parallel, and much greater enhancement seen for B perpendicular (fig. 5.21). Finally, a clear angular dependence of the peak current at 1.5 T is shown in figure 5.22. The maximum peak current for both reduction and oxidation occurs when B is perpendicular to I . Natural convection

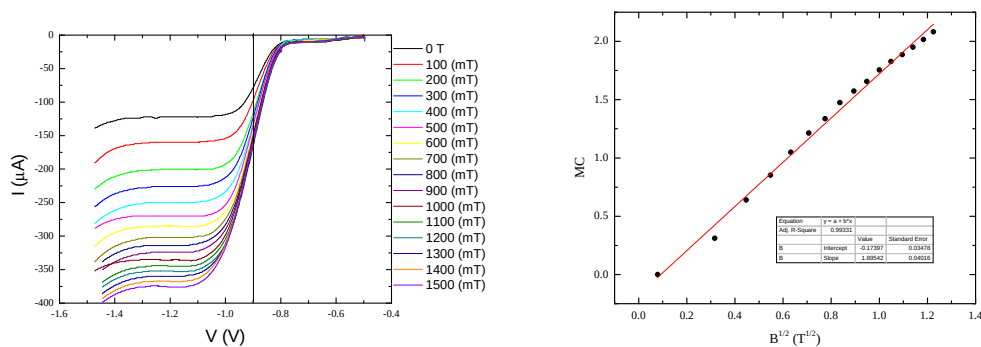


Figure 5.19: (a) Steady state voltammograms under increasing magnetic field (b) magneto-conductance/current enhancement as a function of $B^{1/2}$

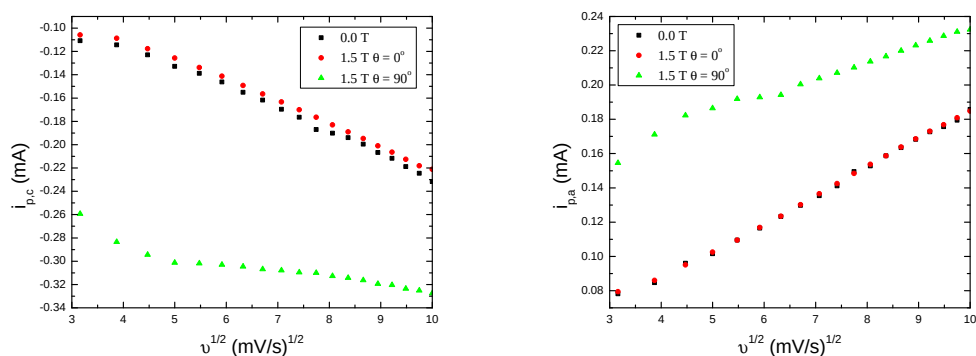


Figure 5.20: Randles-Sevcik plots for (a) reduction and (b) oxidation peak currents under perpendicular and parallel magnetic fields.

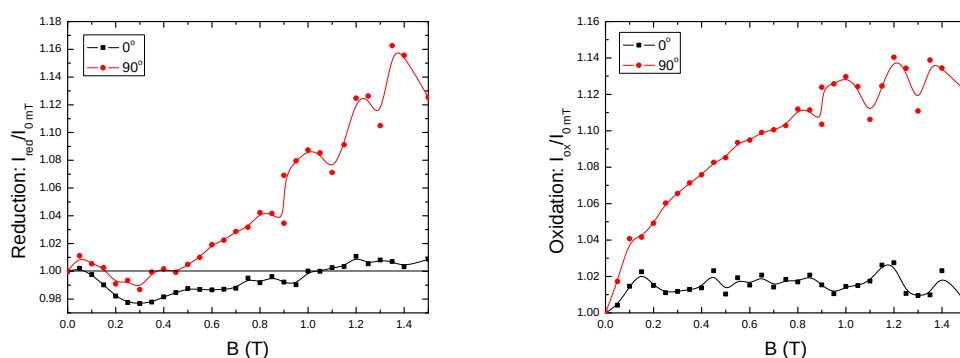


Figure 5.21: Enhancement of peak currents at $v = 100 \text{ mV s}^{-1}$ as a function of applied magnetic field for (a) reduction and (b) oxidation, β -splines are included as guides to the eye.

appears to have little effect as the system is symmetric over 180° . If there was a significant contribution by the natural convection there would be a difference between 0° and 180° as in one direction the Lorentz force would point vertically upwards, and in

the opposite vertically downwards.

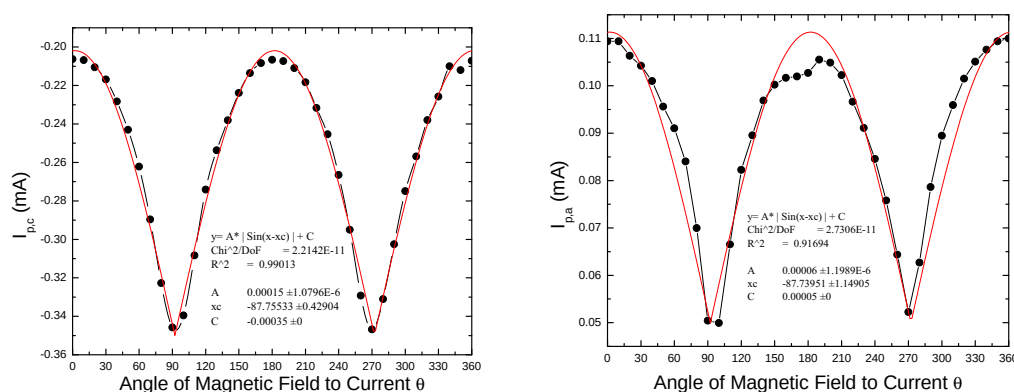


Figure 5.22: (a) Reduction and (b) oxidation peak current as a function of angle between applied magnetic field and nominal current.

A further check was carried out to ensure that there were no angular contributions due to the electrode geometry. At 9 different positions a cyclic voltammogram was measured at 100 mVs with the field on an off. No contribution was seen by rotating the electrodes as shown in figure 5.23, and all effects are due to the Lorentz force.

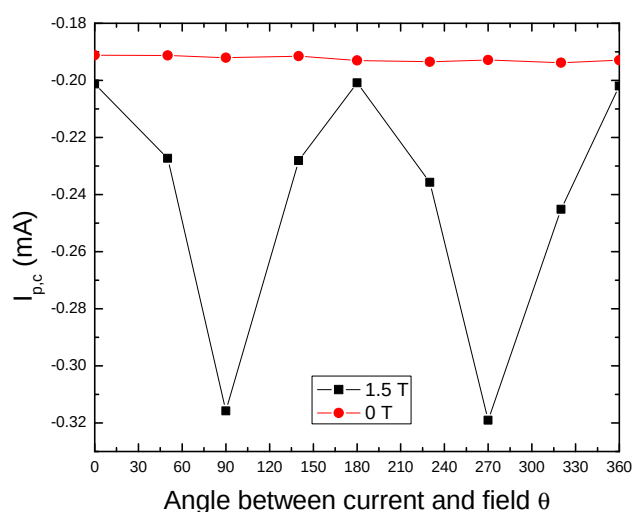


Figure 5.23: Reduction peak current as a function of angle between applied magnetic field and nominal current for the field on and off.

Finally, to highlight the equivalence of Lorentz force stirring and mechanically induced convection, the current response at a 3 mm diameter glassy carbon working electrode as a function of applied magnetic field was compared to that at an RDE also using a 3 mm glassy carbon working electrode as a function of rotation rate. Figure 5.24 shows the reduction peak current at a sweep rate of 100 mV s^{-1} for increasing fields and rotation rate. From this we can determine the application of a 1.5 T field is equivalent to a rotation of 130 rpm. It is important to note that this is true only for this system, e.g.

electrolyte concentration and viscosity; and working electrode area and composition. At a fixed field, the Lorentz force is dependent on the current, and thus the measured current enhancement is also dependent on the coupling between the maximum possible current and the Lorentz force stirring. It can be conjectured that in a more conductive solution, or one with a larger diffusion coefficient, the equivalent rotation rate to a 1.5 T field would be larger than is seen here.

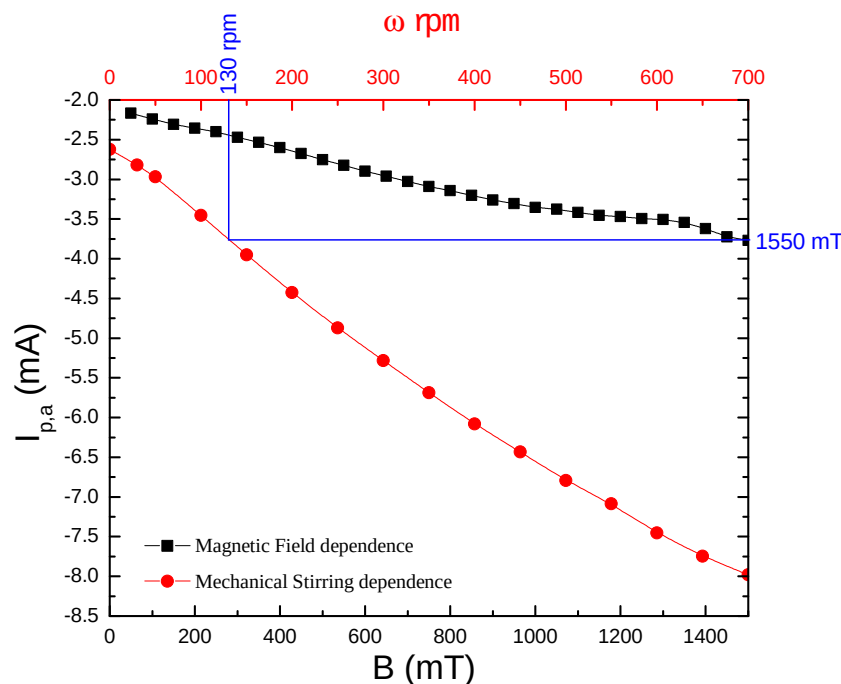


Figure 5.24: Comparison of Lorentz force and mechanical stirring induced current enhancement using a β -spline interpolation.

5.2.2.2 Pulse methods

Cyclic voltammograms mostly give a qualitative description of the mass transport response to the magnetic field. The magnetic field effects on the diffusion layer were further probed using chronoamperometry to monitor the steady-state current, and double step chronocoulometry to explore any magnetic field effect on adsorption. All chronoamperometry measurements were carried out in a 1.5 T magnetic field perpendicular and parallel to the nominal current. As shown in figure 5.25 there is a magnetic field effect on the limiting current in both cases.

When the magnetic field is perpendicular, the current enhancement obeys a power law, as expected for a Lorentz force induced magneto-convection. When the magnetic field is parallel to the current, the current enhancement is linear, and exhibits two regimes. At the working electrode there are edge effects due to non-parallel current lines. These current lines can induce vortex flows at an electrode surface. When the magnetic field is parallel to the nominal current, i.e. perpendicular to the electrode surface these current lines generate a Lorentz force which can stir solution locally and a

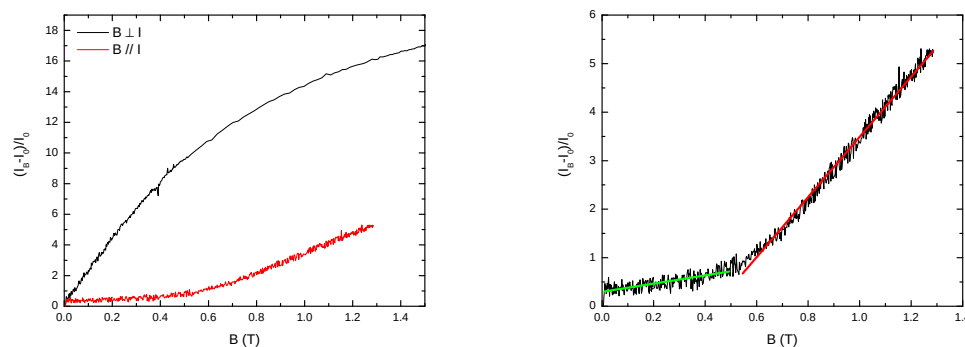


Figure 5.25: (a) Limiting current perpendicular and parallel to B as a function of B , and (b) limiting current parallel to B as a function of B , showing two coupling regimes.

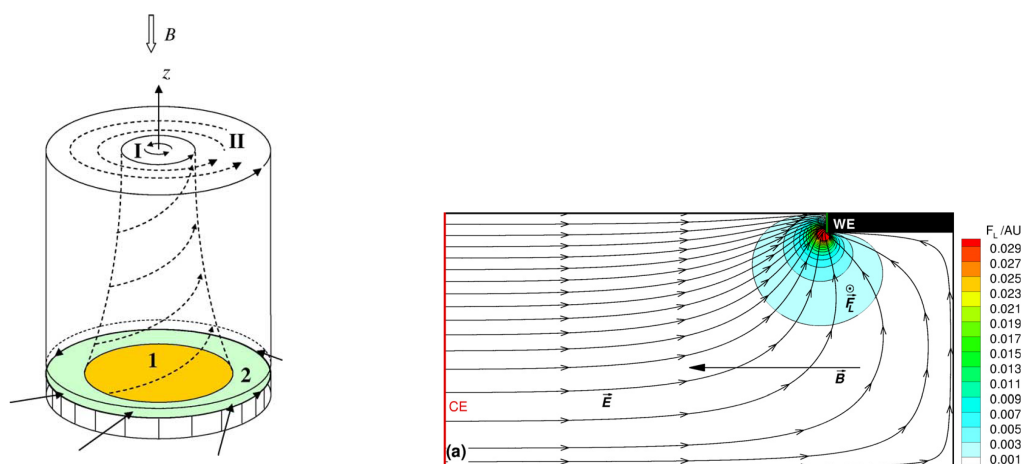


Figure 5.26: (a) Induced vortex flow due to edge currents, initially only region 2 rotates, but as the magnetic field increases, its momentum becomes enough to rotate region 1 too [12] and (b) Lorentz force distribution due to a homogeneous magnetic field and radial currents near a working electrode [13].

vortex flow can form (see fig. 5.26). In this interpretation the first regime in figure 5.25 corresponds to rotation of region 2 in figure 5.26, then once the Lorentz force is large enough, region 2 rotates fast enough to drag region 1 and form a vortex. Extending the analysis of perpendicular magnetic fields to 5 T, and a range of potentials, we can see in figure 5.27 that the limiting current is only enhanced at potentials where NB is actively reduced. Lorentz force stirring is predicated on having moving charges in a magnetic field. The reactant nitrobenzene is neutral, and any Lorentz force on the dipole distribution across the molecule will average to zero. Therefore any Lorentz force effects we see are on the reduced species $\text{NB}^{\bullet-}$, not the neutral molecule.

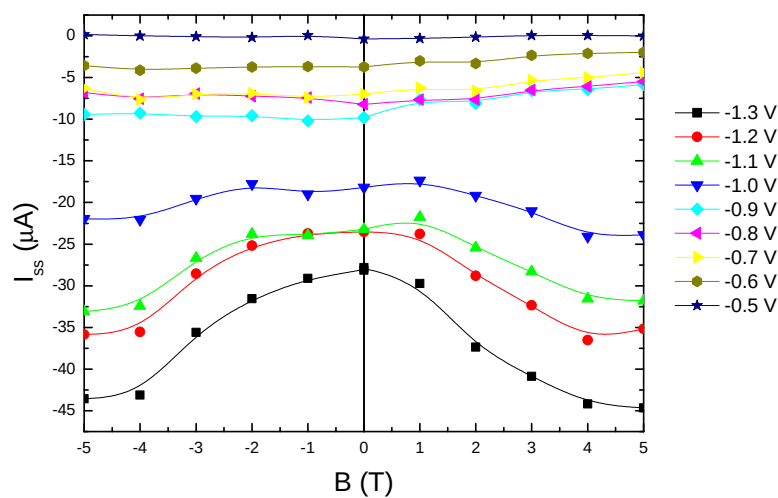


Figure 5.27: Limiting current at a series of potentials and applied magnetic fields, with β -splines used as guides for the eye.

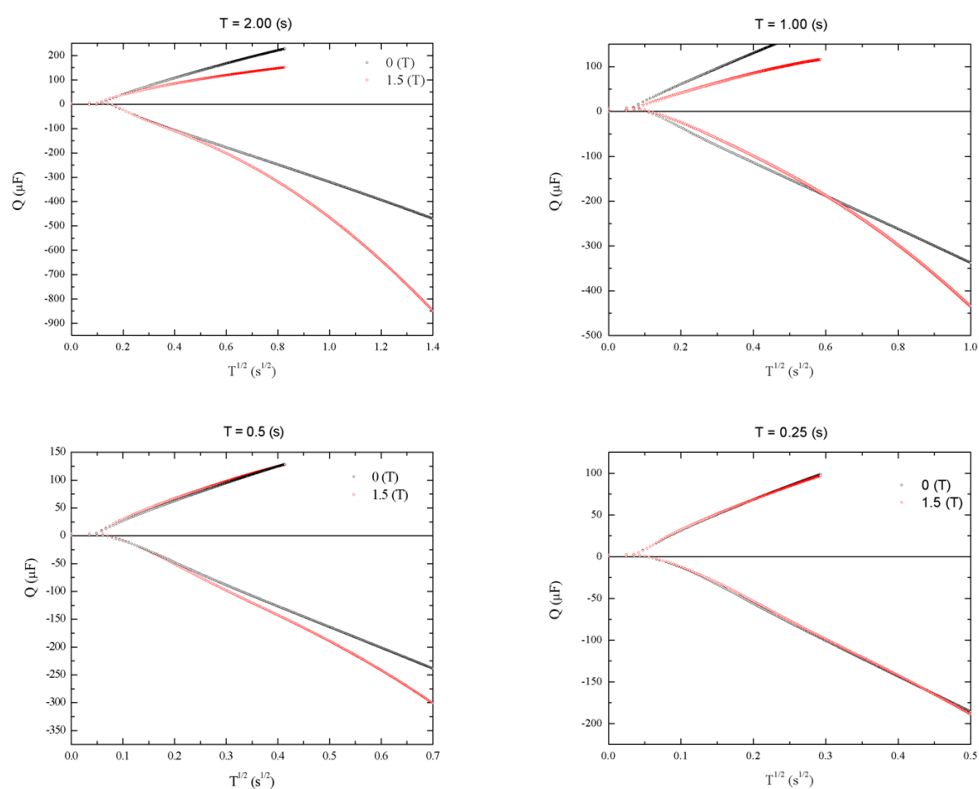


Figure 5.28: Anson plots of charge and discharge of 0.1 M NB for decreasing pulse lengths with and without an applied magnetic field

5. MAGNETOELECTROCHEMISTRY WITH MODEL SYSTEMS

Thus far we have been only concerned with the Lorentz force effects on mass transport. Previously we saw that it is possible to measure the adsorption of $\text{NB}^{\bullet-}$ using double pulse chronocoulometry; and this technique will be employed to illuminate any magnetic field effects. Chronocoulometry is based on the Cottrell equation, and so all assumptions for this model must be satisfied if chronocoulometry is to be used. The primary requirement is that there is no convection at the electrode surface, otherwise the charge is no longer linear with $t^{1/2}$. Of course the application of a magnetic field induces a Lorentz force, and so the pulse length must be shortened such that over the course of the experiment the Lorentz force does not have time to overcome the inertial forces i.e. viscosity of the solution. This is illustrated in figure 5.28 where pulse lengths of decreasing times were used until a linear relationship was found at $\tau = 0.25$ s for an applied field of 1.5 T. Therefore using pulse lengths of 0.25 s we can probe any magnetic field effects inside the diffusion layer without disturbing it.

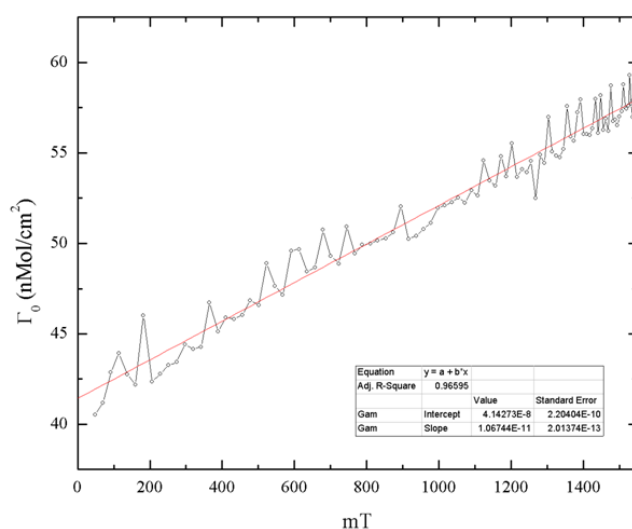


Figure 5.29: Surface adsorption as a function of applied magnetic field.

From the intercepts of the Anson plots, the excess charge on the electrode due to adsorption was seen to increase linearly with applied magnetic field (fig. 5.29). In effect, what we see is an increase in $\text{NB}^{\bullet-}$ concentration in the double layer. Alteration of the double layer by a magnetic field has not been reported before, and asks the question, what is happening in the double layer? Can we influence the double layer structure using the magnetic field, and what consequences will this have on the kinetics of the system, recalling the Fumkin effect from §1.4.5? To answer these questions we must turn to AC impedance methods; double pulse chronocoulometry is limited in that all we can infer from Anson plots is the dependence of adsorption on applied magnetic field, nothing else.

5.2.3 Near Electrode Effects

5.2.3.1 AC Voltammetry

First, to distinguish between the resistive and capacitive contributions of the electrochemical cell, phase-sensitive AC voltammetry can be used. The in-phase response corresponds to the resistive parts of the circuit, and the out-of-phase to the capacitive, which is neatly illustrated in figure 5.30. AC voltammograms were carried out at E_{dc} sweep rates of 10 mV s^{-1} , with an AC amplitude of 25 mV at 100 Hz . Since voltammograms were measured at only one frequency, a fit more complicated than a simple two component equivalent circuit is not possible. The solution resistance was compensated, leaving the response of the charge transfer resistance, Warburg resistance and double layer capacitance subsumed into an equivalent circuit consisting of a resistor and capacitor in series.

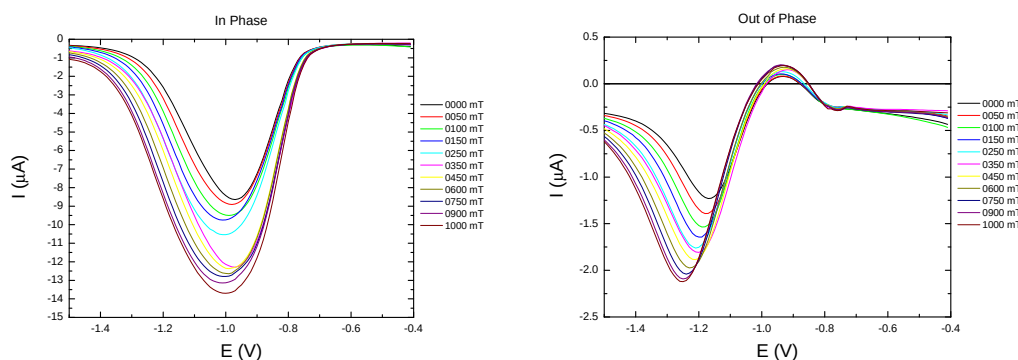


Figure 5.30: AC Voltammograms at 100 Hz for 0.1 M NB as a function of applied magnetic field for (a) in-phase response, and (b) out-of-phase

Figure 5.30.a is essentially the first derivative of a cyclic voltammogram, and the peak corresponds to E^0 . A shift of E^0 with magnetic field would suggest a magnetic field effect on the kinetics of the system, as E^0 is a representation of the thermodynamics of the system, i.e. the Gibbs free energy of the redox reaction, which is

$$\Delta G_0 = -nFE^0 \quad (5.25)$$

No obvious trend was observed for E^0 as a function of B (fig 5.31.a), and any effects are less than the irreproducibility of the measurement. In contrast to E^0 , we do observe an enhancement of the peak current, I_p , (fig. 5.32.a) which is related to the mass transport of the system. The peak current is

$$I_0 = \frac{E_0}{Z_f} = \frac{n^2 F^2 A \omega^{1/2} D^{1/2} c_* E_0}{4RT \cosh^2(a/2)} \quad (5.26)$$

The peak enhancement with B obeys a power-law dependence as expected for MHD

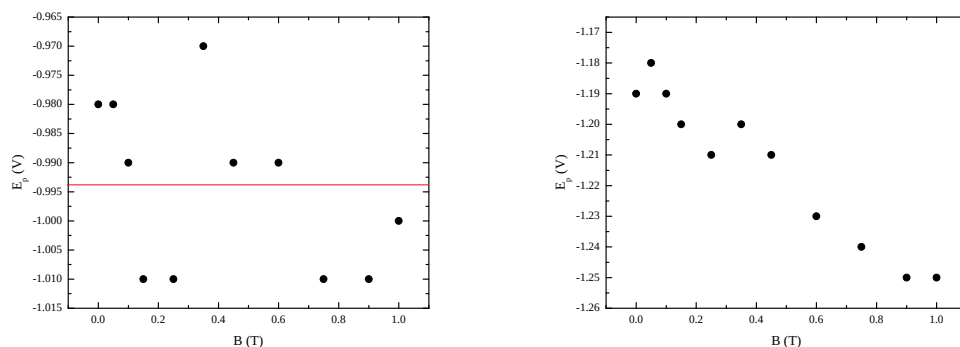


Figure 5.31: Peak potential as a function of applied field for (a) the in-phase response (b) the out-of phase response.

control, giving further support to Lorentz force stirring. Inspecting the out-of-phase current, the situation is more complicated. We can see that magnetic field only begins to have an effect once NB is actively reduced at the electrode, with only minor effects at more positive potentials (fig. 5.30.b). The series peak capacitance is seen to increase logarithmically with applied field (fig 5.32.b), but this effective capacitance masks the effects of both the Warburg impedance (diffusion) along with the double layer capacitance; measurements at two or more frequencies are needed to model a three component circuit.

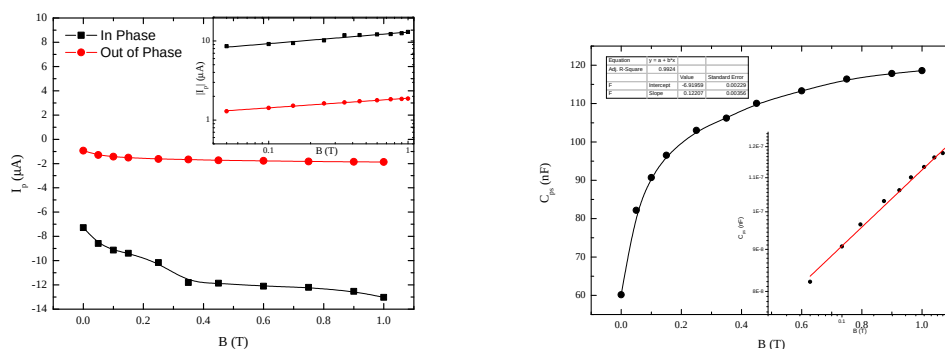


Figure 5.32: (a) Peak current enhancement as a function of magnetic field and (b) enhancement of series peak capacitance with applied magnetic field. Insets are log-log plots.

In the reduction potential window both the position and magnitude of the peak current is dependent on the magnetic field (figs. 5.32.b). The shift in potential is related to the mass transport limited current of the system. The Lorentz force induced convection brings fresh solution to the surface, and will shift the peak potential to more negative values by the Nernst equation

$$E = E^0 + \frac{RT}{nF} \ln a \quad (5.27)$$

where $a = C_O/C_R$ is the ratio of NB concentration to $\text{NB}^{\bullet-}$. The magnetic field induced peak shift ΔE_p can be related to the concentration ratios by

$$\exp\left(\frac{\Delta E_p n F}{RT}\right) = \frac{a_B}{a_0} \quad (5.28)$$

where a_B and a_0 are the concentration ratios under an applied magnetic field and at zero field respectively.

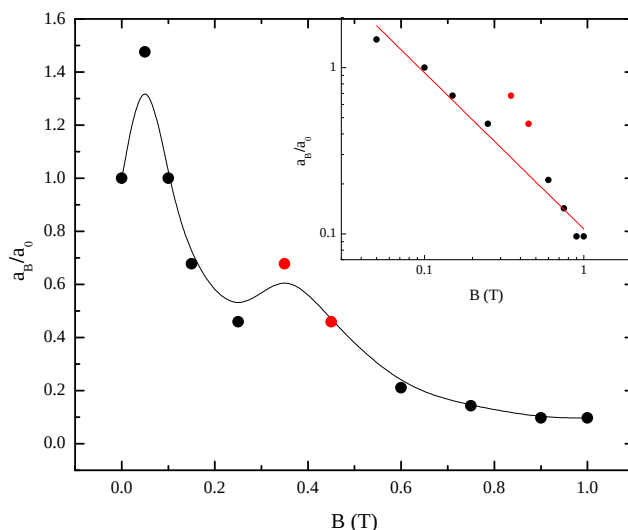


Figure 5.33: Relative change in concentration ratio as a function of applied magnetic field. Inset is a log-log plot.

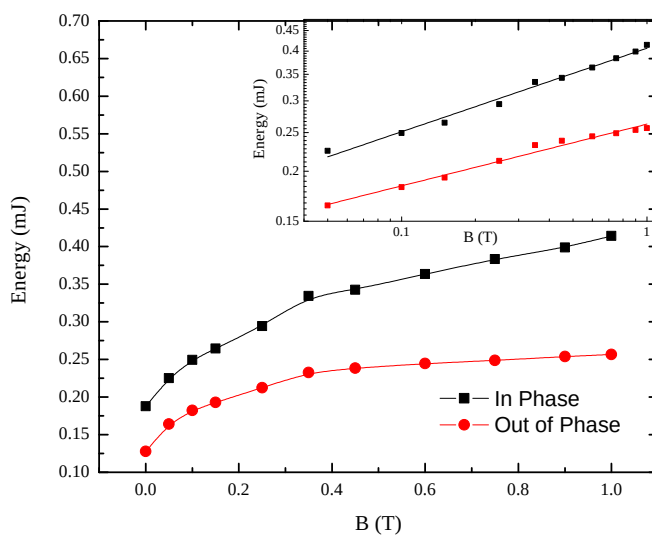


Figure 5.34: In-phase and out-of-phase energy consumption as a function of applied field. Inset is a log-log plot.

In agreement with the chronocoulometry measurements, the relative amount of $\text{NB}^{\bullet-}$ increases

with applied magnetic field, as seen in the relative decrease in concentration ratio shown in figure 5.33. Finally, for both the in-phase and out-of-phase currents, the peak areas increased; which is another way of saying the power, or energy output increased (fig. 5.34). This is a transfer of energy from the magnetic field to the electrochemical system, through the enhanced mass transport, and increased adsorption. To further differentiate these effects, and overcome the limitations of AC voltammetry, it is important to now focus on impedance spectroscopy methods.

5.2.3.2 Impedance Spectroscopy

Impedance spectroscopy allows us to study fast processes such as the kinetics and double layer charging, along with longer timescale phenomena such as mass transport effects all in one experiment. Measurements were carried out in both the 5 T and 1.5 T magnets using a 0.5 mm diameter Pt disc working electrode as before. The magnetic field was applied perpendicular to the current in both cases.

First studying the impedance spectra close to the reduction potential, figure 5.35 shows the three potentials chosen to measure impedance spectra at on a series of cyclic voltammograms. The reduction potential, and two other less negative potentials close to E^0 and E_{pzc} were chosen to get the greatest measurable response from the double layer.

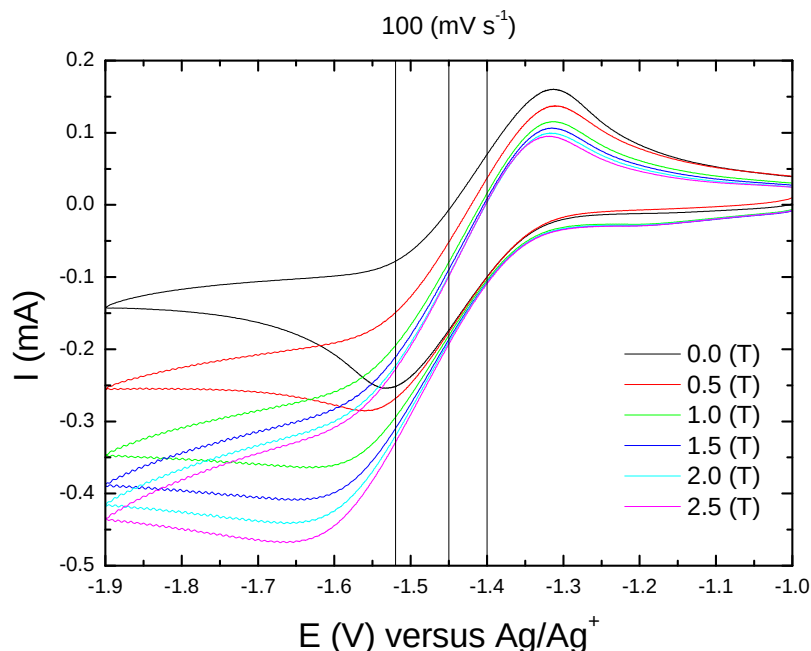


Figure 5.35: Cyclic voltammograms of 0.1 M NB at 100 mV s^{-1} over a range of magnetic fields.

Nyquist plots at the reduction potential in figure 5.36 show the evolution of the electrochemical system with increasing magnetic fields. The semicircle corresponds to the

high frequency response of the charge transfer resistance and double layer capacitance RC, and the low frequency lines represent the Warburg diffusion impedance Z_W .

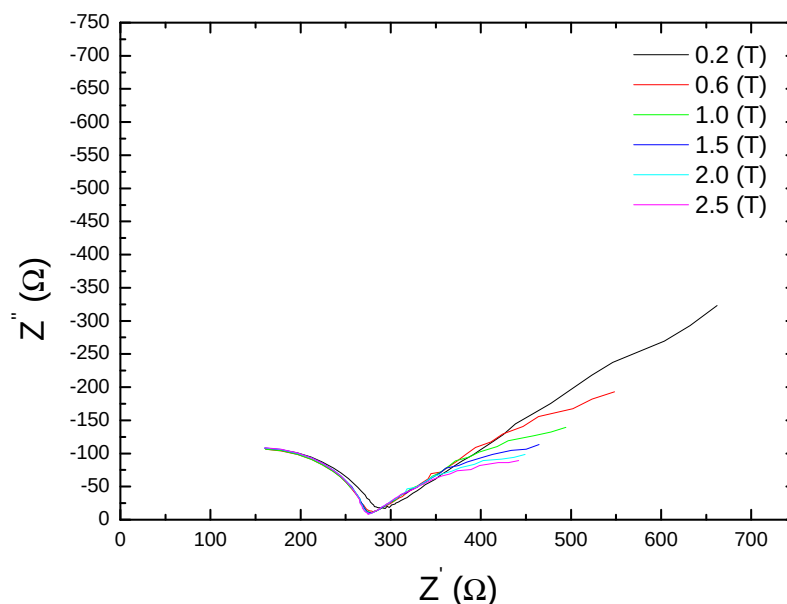


Figure 5.36: Impedance spectra of 0.1 M NB at the reduction potential for a series of magnetic fields.

The low frequency response follows a power law dependence of the Warburg impedance with B in agreement with all previous data on the mass transport of the system (fig. 5.37.a), and a thinning of the diffusion layer by Lorentz force stirring (fig. 5.37.b). The weakest response of Z_w to the magnetic field is for the most positive potential, where the current is kinetically controlled, conversely, the greatest coupling is at the reduction potential under mass transport control, as expected for a Lorentz force effect, which upon inspection agrees with observed currents in figure 5.35 where there is little effect on the I-V curves in this potential region.

The most striking results, however are at high frequencies, where the double layer and charge transfer resistance show a clear power-law dependence on the applied magnetic field (fig. 5.37). At the reduction potential, a decrease in double layer capacitance is observed, and at more positive potentials the double layer capacitance is either unaffected or increases. For the double layer capacitance to decrease with applied field, treating it as a Helmholtz capacitor, either the relative permittivity decreases or the double layer thickness increases. An increase in thickness is congruent with the observed increase in adsorption as the relative permittivities of NB and acetonitrile very similar (see table 5.1) and a change in their relative concentrations at the electrode surface will not generate the required change in double layer capacitance. There have also been studies to show that the magnetic field effect on the relative permittivity

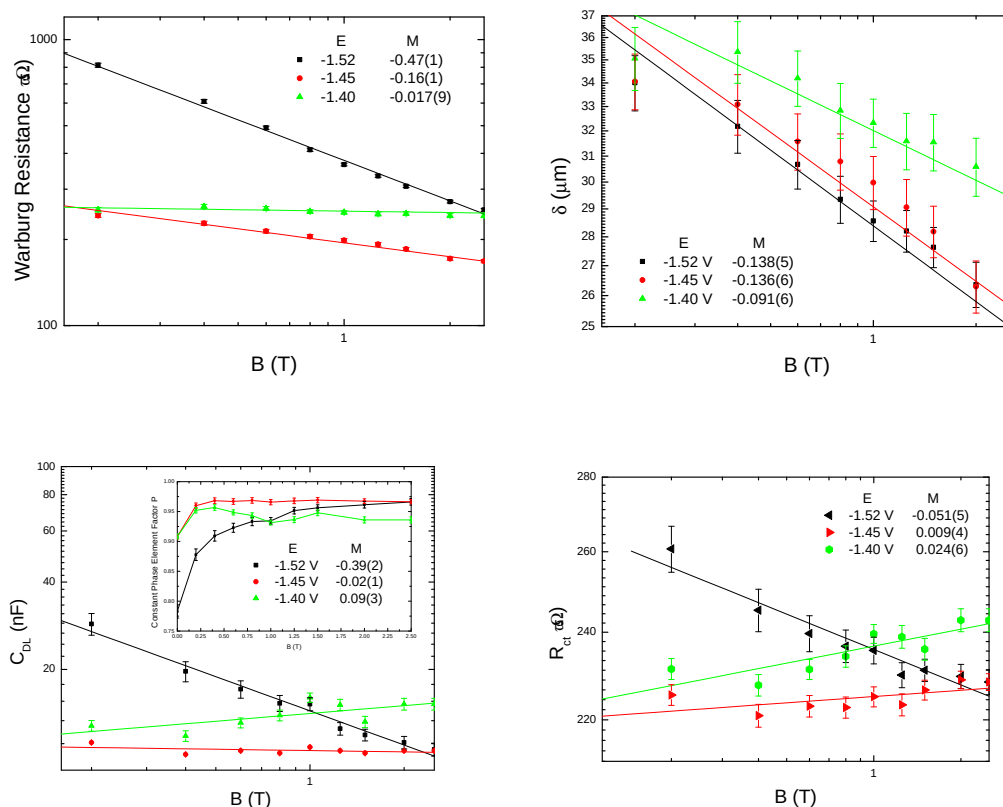


Figure 5.37: The magnetic field dependence of (a) the Warburg resistance, (b) diffusion layer thickness, (c) double layer capacitance and CPE ideality factor, and (d) charge transfer resistance.

of nitrobenzene, along with other materials, is on the fourth or fifth significant digit [14] and is therefore completely negligible as a primary source of capacitance change observed in the double layer.

The opposite effect is measured at the most positive potential, which suggests that even in the double layer, all the magnetic effects arise from the interaction of $\text{NB}^{\bullet-}$ with the magnetic field. The double layer capacitor was fitted with a constant phase element (CPE) to model the effect of a distribution of capacitances at the electrode surface due to roughness. For a smooth surface the ideality factor is $N = 1$, and for a porous electrode it is $N = 1/2$; values less than 1 give a measure of the electrode roughness, and the broadness of the double layer thickness distribution (see §1.4.2). At the reduction potential the ideality factor tends to 1 with increasing applied magnetic field, and at the most positive potential decreases with increasing field and capacitance; supporting the claim that it is the double layer thickness that is being altered as the surface roughness perturbation effect diminishes with thicker layers. The measured charge transfer resistance follows the same trends as the capacitance, decreasing at the reduction potential, and increasing elsewhere. As we argued earlier, and saw in the AC in phase

voltammograms, the magnetic field has no direct influence on the thermodynamics of the system, therefore the alteration of the charge transfer resistance must be linked to the structural changes in the double layer. This can be accounted for using the Frumkin correction discussed in §1.4.5.

For the reduction of NB, the ions closest approach is to the electrode is the OHP (Outer Helmholtz Plane). The potential at the OHP, ϕ_2 , is not the same as in the bulk solution, ϕ_s because of the potential drop across the diffuse layer, and this difference manifests itself in two ways. The first is the concentration of the reactant at the OHP is different to the bulk value

$$C_{OHP} = C_{\infty} \exp \left(-\frac{z_i F \Delta \phi_2}{RT} \right) \quad (5.29)$$

Second, the driving force for the electrochemical reaction is the potential difference between the electrode and the reacting site. At the OHP this value is different, and the apparent kinetic rate constant for the reduction reaction needs to be corrected thus:

$$k_c = k_{0,t} \exp \left[\frac{-\alpha_c n F (\phi_M - \phi_2)}{RT} \right] \quad (5.30)$$

and hence the exchange, or kinetic, current becomes

$$i_0 = i_0^{exp} \exp \left[\frac{-\alpha_c n F (\phi_M - \phi_2)}{RT} \right] \quad (5.31)$$

Qualitatively, these statements agree with observation, as we increase the magnetic field, the double layer thickness, and $\text{NB}^{\bullet-}$ -adsorption increase, both of which suggest that the OHP is driven closer to the electrode surface, thus increasing the potential seen by the molecules and the measured kinetic constant.

A simple phenomenological model can explain these effects in a consistent manner. First we assume the same double layer structure as developed in §5.2.1.4; consisting of (i) a Helmholtz geometric capacitance, (ii) the diffuse double layer capacitance from the supporting electrolyte and solvent, (iii) a diffuse layer pseudo-capacitance dependent on $\text{NB}^{\bullet-}$ that only appears at potentials more negative than E^0 of the system, and (iv) the coupling of ion non-specific adsorption to the electrode potential. The same assumptions were employed as before, which also have the same limitations such as the masking of recombination currents and surface roughness, and a failure to correctly model the capacitance close to the pzc.

Next, we need to introduce the magnetic interactions in the system. In the double layer during the reduction of NB, a $\text{NB}^{\bullet-}$ -phase is formed close to the electrode surface, at the OHP, diffusing into the diffuse double layer. This may be viewed as a mixed, but separate phase in the solution with a net paramagnetic susceptibility. The $\text{NB}^{\bullet-}$ -phase

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forms in the double layer, deep inside the diffusion layer, and so is unaffected by the Lorentz force-induced thinning of the diffusion layer by magneto-convection. The magnetic field gradient force can also be neglected as all measurements were carried out in uniform magnetic fields (0.1 % in a 10 mm DSV). This would lead one erroneously to the conclusion that there is no magnetic field effect in the double layer.

If we treat the interaction in terms of energy, in the presence of a magnetic field the total energy of the $\text{NB}^{\bullet-}$ phase is increased by the magnetostatic energy $E = 1/2\mu_0\mathbf{M} \cdot \mathbf{H}$. Using the magnetic charge model this can be represented as sum of fictitious magnetic charges q_m at the interface, with a force on each magnetic charge $\mathbf{f} = \mu q_m \mathbf{H}$. There is no *net* force, as a surface integral of the charge forces will sum to zero, but there is still a change in the energetics of the system. Instead, the $\text{NB}^{\bullet-}$ phase experiences a stress, referred to as the Maxwell stress. In §2.6 we showed that the Maxwell stress describes the total electromagnetic energy of a system as a surface stress. In this view the magnetostatic interaction energy is just part of the total stress on the system:

$$T_{ij} = \epsilon_0 E_i E_j + \frac{1}{\mu} B_i B_j - \frac{1}{2} (\epsilon_0 E^2 + \frac{1}{\mu} B^2) \delta_{ij} \quad (5.32)$$

where ϵ is the material permittivity, μ is the material permeability, and δ_{ij} is Kronecker's delta. Continuing with the magnetic charge analogy, the force $\mathbf{f}$ acts to lower the energy of the system by increasing the distance between each magnetic charge through a force normal to the phase surface $\mathbf{f} = \mu q_m \mathbf{H}$. The total surface energy of the system can be written as a sum of the chemical surface energy, the energy of the electric field due to the excess charges, and the magnetostatic energy of the paramagnetic species in a magnetic field, (assuming full coverage):

$$E_t = A_d \gamma_{\text{NB,Pt}} + S_{\text{NB}} \gamma_{\text{NB,SE}} - A_c \gamma_{\text{SE,Pt}} - \frac{1}{2} C V^2 - \frac{1}{2} \mu_0 \chi B^2 \text{vol} \cos(2\theta) \quad (5.33)$$

where A_d is the contact area, and $\gamma_{\text{NB,Pt}}$, the surface tension between the $\text{NB}^{\bullet-}$ phase and the Pt electrode; S_{NB} is the surface area of the $\text{NB}^{\bullet-}$ phase, $\gamma_{\text{SE,Pt}}$ is the surface tension between the $\text{NB}^{\bullet-}$ phase and the supporting electrolyte, A_c is the contact area between the supporting electrolyte and the Pt electrode, $\gamma_{\text{SE,Pt}}$ is the surface tension between the supporting electrolyte and the Pt electrode, C is the double layer capacitance, V is the electrode voltage relative to the point of zero charge, μ_0 is the permeability of free space, χ is the molar susceptibility of the $\text{NB}^{\bullet-}$ phase, c is the concentration of $\text{NB}^{\bullet-}$, B is the external magnetic field and vol is the volume of the $\text{NB}^{\bullet-}$ phase.

There is a complex interplay between the electrode charge, the magnetostatic energy, and the surface tension. Surface tension is an important parameter in the double layer; the Lipmann equation [8] states that the surface tension on the electrode is related to the charge by

$$\frac{\partial \gamma}{\partial E_\Delta} = -\sigma_m / A_e \quad (5.34)$$

where γ is the surface tension, E_{Δ} is the potential drop across the metal/solution interface, σ_m is the charge on the electrode, and A_e is the electrode area. This in turn is related to the measured differential capacitance in the impedance measurements by

$$\frac{\partial \sigma_m}{\partial E_{\Delta}} = C_d \quad (5.35)$$

This shows that the point of zero charge (pzc) appears at a minimum of the capacitance voltage curve. The importance of the Lipmann equation is that both the charge and capacitance are dependent on the surface tension. The Maxwell stress influences the surface tension in two ways, first is through the magnetostatic energy term, and the second is the alteration of the ion concentration at the electrode surface by the phase deformation, which changes the excess charge at the electrode, thus altering the electrostatic energy. Therefore we would expect an increase in total surface energy with the applied magnetic field parallel to the surface and a decrease for perpendicular to the surface. This is because the application of a parallel magnetic field leads to an increased contact area, and to increase the contact area, we need to increase the energy of the system. As a corollary to this, the same effect is to lower the surface tension (remembering the stresses are a result of the negative gradient of the energy).

At this juncture it is important to point out that length scales involved in the magnetostatic and electrostatic energies have to be considered carefully. We recall that the diffusion layer is defined as the region close to the electrode that is rich in the electrochemical product and poor in the reactant. In practise this means we have a concentrated spheroid region of $\text{NB}^{\bullet-}$ ‘hanging’ between the end of the diffuse double layer and the end of the diffusion layer. The magnetostatic energy acts across this entire volume, and so the thickness t in (5.33) is the thickness of the diffusion layer. This introduces extra complexity to the model, as we observed that the Lorentz force influences the thickness of the diffusion layer, which must be taken into account. To this end, to account for the electrostatic energy, the total charge in the diffusion layer needs to be considered, rather than just the integral of the double layer capacitance. However, a simplification is possible as almost all of the potential drop occurs in the double layer, the volume integral of the charge density will vary only slightly from that at the electrode surface, allowing us to use the representation chosen in (5.33).

Two cases are considered (shown in fig. 5.38), the first is when a magnetic field is applied parallel to the surface, corresponding to figure 5.38.a & c. The induced magnetisation, represented by fictitious magnetic charges are repulse from each other, and to minimise the energy of the system a prolate deformation occurs, i.e. the $\text{NB}^{\bullet-}$ phase expands in the plane parallel to the electrode surface, while thinning in the perpendicular direction. This in turn leads to a decrease in surface charge, as the number of $\text{NB}^{\bullet-}$ ions increases due to the deformation, which in this case means the surface charge becomes less negative. The decrease in surface charge then couples with the electric

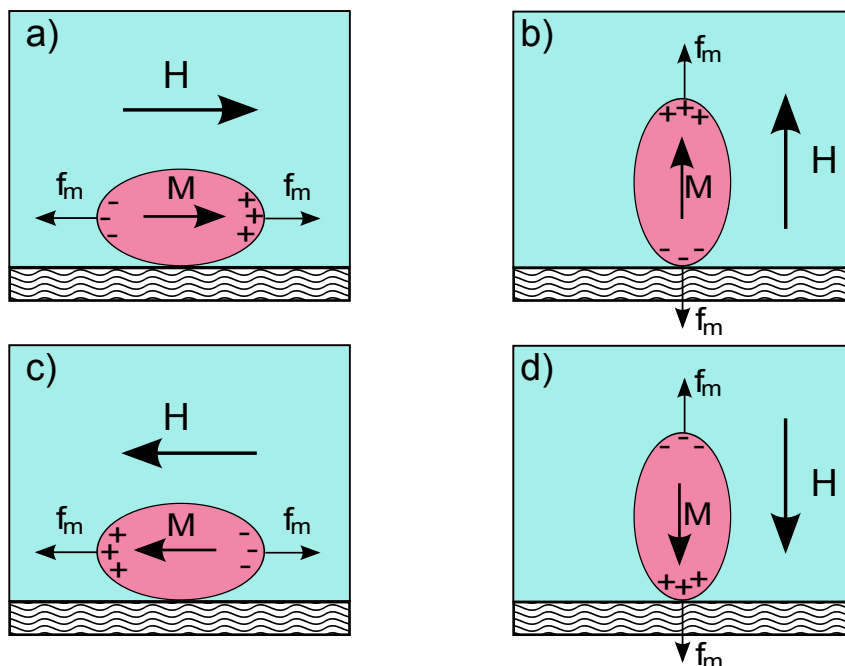


Figure 5.38: The deformation of a net paramagnetic liquid at an electrode surface due to Maxwell stresses. (a) & (c) show the case when the magnetostatic forces are greater than those from the electrostatic field in the z -direction, (b) & (d) show the case when the magnetostatic forces are less than the electrostatic forces in the z -direction.

field, decreasing the surface tension further. In case 2 (figs. 5.38.b & d), where we apply the magnetic field perpendicular to the electrode surface, the magnetisation deforms the $\text{NB}^{\bullet-}$ phase in an oblate fashion. The magnetostatic energy still lowers the total surface energy in equation (5.33), however the electrostatic response is now quite different. The oblate distortion raises $\text{NB}^{\bullet-}$ ions away from the electrode surface, effectively increasing the electrode charge, in this case making it more negative. This causes the electrostatic reduction of the surface tension to decrease with increasing magnetic field.

In summary, for the parallel case we expect the total surface energy to decrease –the ellipsoidal phase widens (oblate) and gets closer to the electrode surface– and we expect the coupling to be greatest at negative potentials where $\text{NB}^{\bullet-}$ exists. For the perpendicular case, the ellipsoidal phase stretches away from the surface (prolate), raising the total surface energy, with the greatest effect also at negative potentials. Intuitively one would also expect this effect to be weaker for the perpendicular case, as the magnetostatic energy will be working in the opposite direction to the electrostatic energy.

What are the consequences of this model, and are there any testable predictions? First we expect to see an effect for only paramagnetic solutions, diamagnetic solutions will experience a small pressure increase, a few orders of magnitude smaller than the stress experienced by paramagnetic ones. The prolate-like deformation will decrease the surface tension of paramagnetic liquids, thereby decreasing the total surface charge and capacitance. The deformation will also increase the adsorption of $\text{NB}^{\bullet-}$ at the electrode

surface as the phases' volume will be drawn closer to the electrode and thinner. This will appear as a shifting of the pzc with applied magnetic field, reflected by the Esin-Markov effect. The charge transfer resistance will also decrease with applied magnetic field through the Frumkin effect –the potential at the OHP depends on the distance to the electrode– which will increase for decreasing distances from the electrode. Finally, while the forces on the magnetic charges scale with $|\mathbf{H}|$, or $|\mathbf{B}|$, the total energy change, i.e. change in surface tension, scales with B^2 , so the capacitance also be expected to have a power law dependence on B , and should be independent of the sign of the magnetic field. Finally, as already stated, we expect the greatest magnetic field effect to occur when the magnetic field is applied parallel to the electrode surface.

To test these hypotheses two kinds of measurements were carried out, first capacitance-voltage (C-V) and resistance-voltage (R-V) curves were measured at a fixed frequency of 10kHz for a range of magnetic fields, then the capacitance and resistance was measured at a fixed frequency and voltage while sweeping the field. Finally two comparison diamagnetic systems were studied as a null hypothesis.

5.2.3.3 Model Validation

The first test of the model involves studying the field dependent effects on the capacitance-voltage curves (fig. 5.39) of the double layer in the surface parallel case (figs. 5.38.a & c). There is little effect on the diffuse layer capacitance by the magnetic field at more positive potentials, most of the effects are concentrated at potentials more negative than the pzc, where NB is actively reduced; in agreement with all our previous observations. We can also see in figure 5.39 that the three capacitor model outlined previously was used to fit the data, and the fitted response of the C-V curves to an applied magnetic field agrees well with the data (figs. 5.39 a & b). The centre-of-mass pzc, defined as the global minimum on the C-V curve, and following this trend the pzc of $\text{NB}^{\bullet-}$ (the more negative peak) relative to the global pzc shifts in the negative direction (fig. 5.41.e), indicative of increased $\text{NB}^{\bullet-}$ adsorption with the magnetic field, and the concentration of $\text{NB}^{\bullet-}$ in the diffuse layer was seen to increase with magnetic field (fig. 5.41.d).

Together these two observations characterise an increased attraction on the $\text{NB}^{\bullet-}$ ions to the electrode surface, in agreement with our model. The same effect is observed for the supporting electrolyte/solvent double layer contribution, the pzc shifts in the positive direction with increasing B , which is most likely due to an increased adsorption of TBA^+ requiring a more positive potential to attract negative ions to balance the charge at the surface. Furthermore, the ion concentration (TBA^+) increases with field, in agreement with this observation. Both pzc shifts are linear in field, thus the adsorption must also be linear with field, as was observed in the double pulse

chronocoulometry. It is also possible to observe the effects of both species in the compact layer, where the Helmholtz capacitance decreases with magnetic field (fig. 5.42.b), and as argued earlier this is due to an increase in the compact layer thickness. It is also interesting to note the ideality factor for TBA^+ remains mostly unchanged with field, we do not observe an introduction of a recombination current, and the surface roughness and electrode surface potential distribution remains unaffected by the applied magnetic field; no coupling would be expected. $\text{NB}^{\bullet-}$ behaves in a different manner, the ideality factor decreases with the magnetic field, informing us that the net recombination current in the double layer increases. This is not an unreasonable effect; the protonation current is a first order homogeneous chemical reaction, which is dependent on the $\text{NB}^{\bullet-}$ concentration, as we observed in §5.2.1. Finally, there is an observed increase in non-specific adsorption with magnetic field (fig. 5.42.a), caused by the increased ion concentration in the diffuse and compact layers, and consistent with the other extracted parameters.

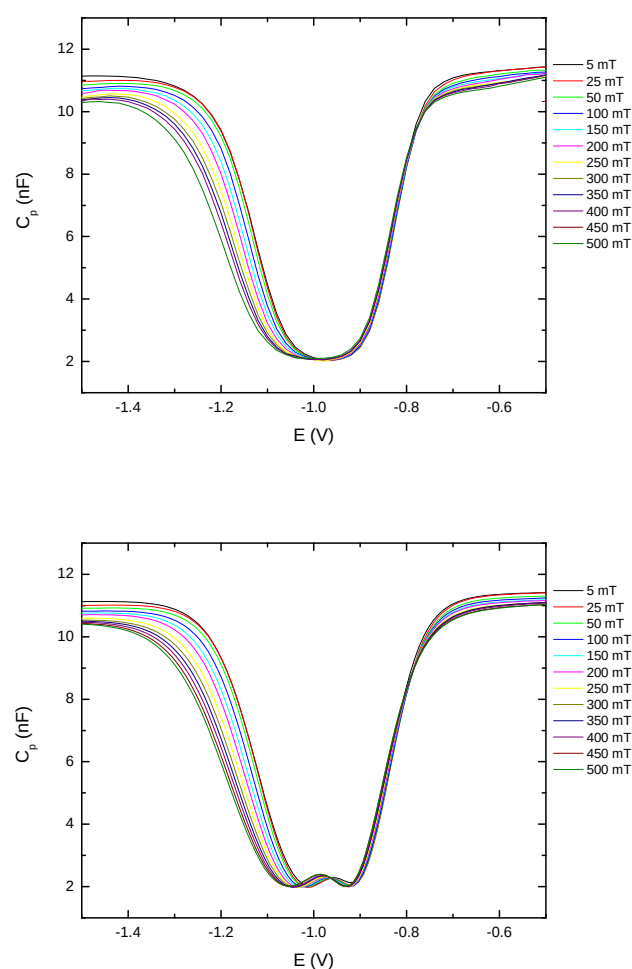


Figure 5.39: Capacitance-voltage curves for 0.1 M NB at 10kHz (a) measured data and (b) theoretical fits

To further probe the double layer, the capacitance-voltage curves were integrated to

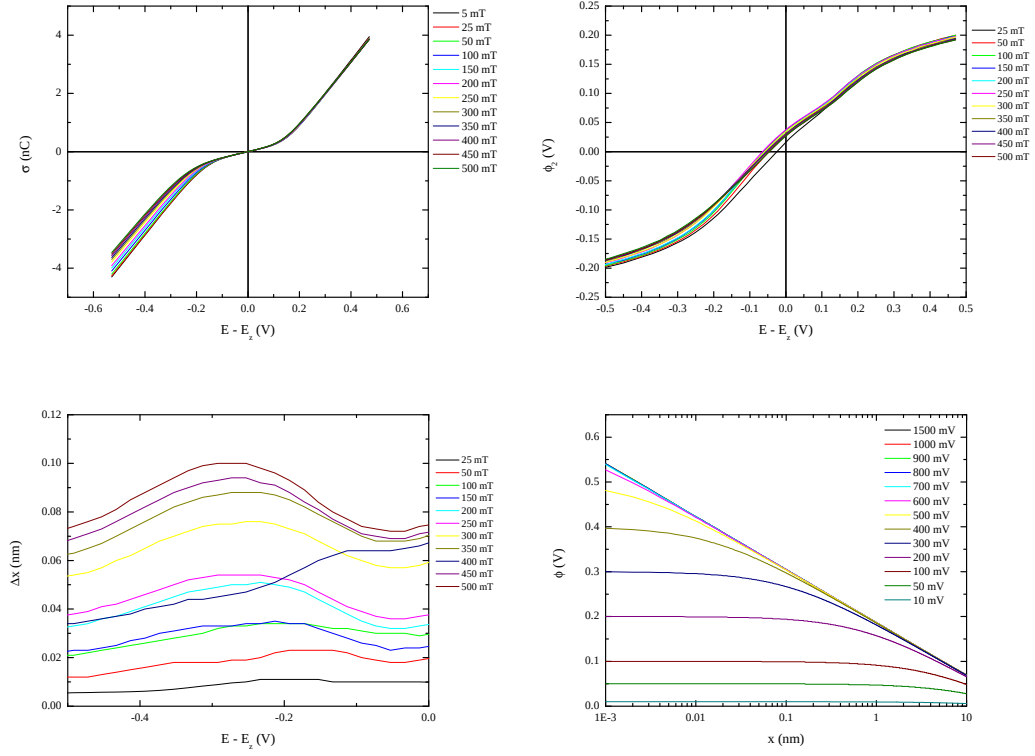


Figure 5.40: (a) Electrode charge -voltage curves for 0.1 M NB at series of applied fields, (b) OHP potential at a series of magnetic fields, (c) change in OHP position towards the electrode as a function of potential and field, and (d) potential profile of the solution in the double layer for a series of electrode potentials.

generate a series of charge-voltage curves. The data was adjusted to compensate for the global pzc, and noting that at this potential the charge is zero, to integrate the data correctly (fig. 5.40.a). From this the potential in the diffuse layer at the OHP was calculated by the rearrangement of

$$\sigma_m = \sqrt{8k_b T \epsilon_r \epsilon_0 n_i^0} \sinh \left(\frac{ne\phi_2}{2k_b T} \right) \quad (5.36)$$

where k_b is Boltzmann's constant, ϵ_r is the relative permittivity of the solution/ion mix, ϵ_0 is the permittivity of free space, n_i^0 is the ion number density, n is the charge number of the ion, and T is the solution temperature; to

$$\phi_2 = \frac{2k_b T}{ne} \sinh^{-1} \left(\frac{\sigma_m}{\sqrt{8RT\epsilon_r\epsilon_0 c_i}} \right) \quad (5.37)$$

where R is the gas constant, and c_i is the ion concentration in the diffuse layer. The change in OHP distance towards the electrode was then calculated using the relation

$$\frac{\tanh(ne\phi/4k_b T)}{\tanh(ne\phi_2/4k_b T)} = \exp[-(x - x_2)/x_{DL}] \quad (5.38)$$

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where ϕ is the potential at a distance x from the electrode surface, ϕ_2 is the potential at the OHP, which lies at a distance x_2 from the electrode, and x_{DL} is the characteristic thickness of the diffuse double layer, i.e. its Debye length.

$$x_{DL} = \left(\frac{\epsilon_r \epsilon_0 k_B T}{2n_i^0 n^2 e^2} \right)^{1/2} \quad (5.39)$$

When comparing the relative change in OHP spacing the above equation can be rewritten as

$$\Delta x = -x_{DL} \exp \left[\frac{\tanh(ne\phi_2^0/4k_b T)}{\tanh(ne\phi_2^B/4k_b T)} \right] \quad (5.40)$$

where ϕ_2^0 is the OHP potential in zero field, and ϕ_2^B is the OHP potential under a magnetic field B.

The concentration of $\text{NB}^{\bullet-}$ in the diffuse layer extracted from the C-V graphs was used to calculate this spacing, which is only valid for potentials less than the pzc, where NB reduces. What we can clearly see is that the distance from the OHP to the electrode surface, or IHP decreases with B. The change in spacing is less than $1\text{\AA}$ at 500 mT, and $< 0.1\text{\AA}$ at 25 mT (fig. 5.40.c), which are very small changes in position. However, the potential gradient in the double layer is huge, figure 5.40.d shows the calculated potential profiles in the double layer for a series of electrode potentials. The majority of the potential drop occurs in the first few nanometres, so even a fractional decrease in the distance to the surface can lead to a much higher potential at the OHP. Calculations were also carried out on the magnetic field effect on the potential profile in the double layer to separate any effects from an OHP movement, and a potential profile change. Potential profile as described by (5.38) were calculated using the $\text{NB}^{\bullet-}$ concentration values extracted from the capacitance-voltage curves. Almost no effect was observed on the potential profiles (fig. 5.43), therefore movement of the OHP closer to the electrode surface does not distort the potential profile in any meaningful way; and is the source of the significantly lowering of the charge transfer resistance with B.

Indeed this effect is observed in resistance-voltage curves extracted from the same impedance data sets at the C-V curves (fig. 5.44.a), which can also be viewed in terms of the measured kinetic constant k^0 (fig. 5.44.b). From the C-V data, the greatest field effect is at voltages less than the pzc, where NB is actively reduced. Inspecting the dependence of k^0 with field, at the most negative potentials the kinetic rate constant is enhanced by 20% in 0.5 T, and closer to the pzc, this increases to 46% enhancement.

Returning to the surface tension response, fig. 5.50 highlights the complex interplay of the magnetostatic energy, electrostatic energy, and surface tension mentioned. The maximum surface energy (tension times area) is $\approx 0.7\text{ nJ}$ at 0 T (fig. 5.50.a). There is a strong coupling of the surface energy to the magnetic field, showing that the magnetostatic interaction is quite important. The greatest effect is observed for potentials negative of the point of zero charge, i.e. the regions where concentrated $\text{NB}^{\bullet-}$ exists in

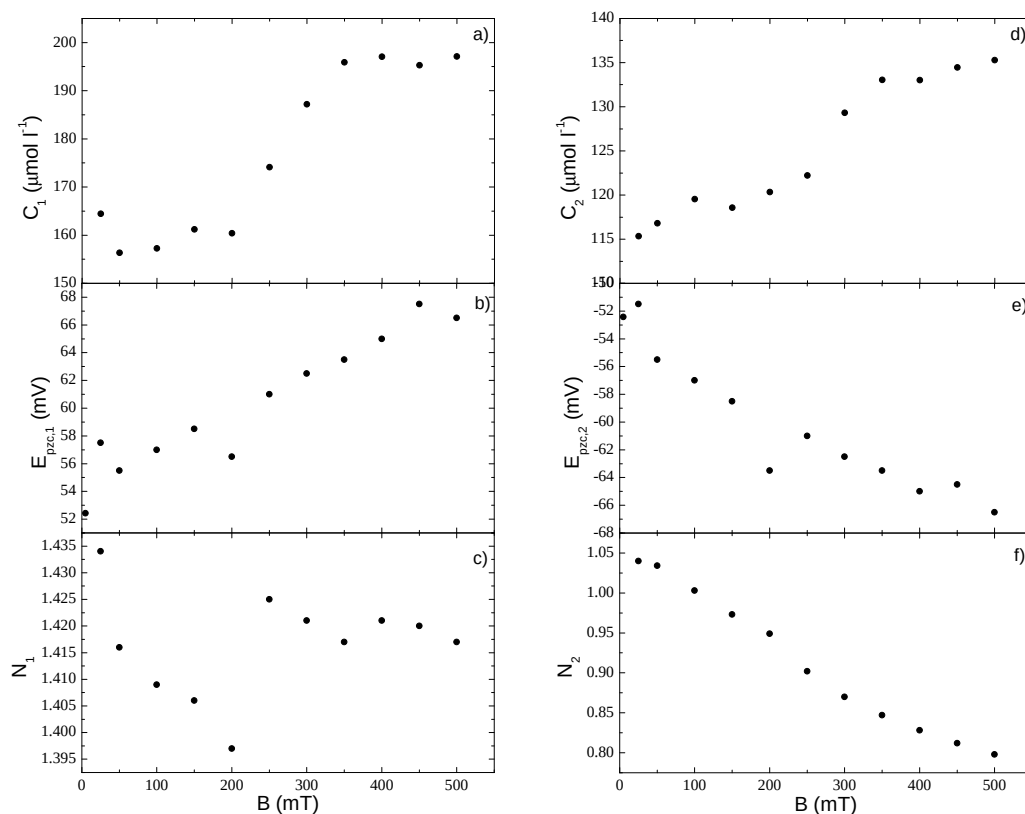


Figure 5.41: $B \parallel$ surface: TBA^+ : (a) Concentration in the diffuse layer, (b) pzc relative to the global pzc, and (c) ideality factor relative to the applied magnetic field. **$\text{NB}^{\bullet-}$:** (d) concentration in the diffuse layer, (e) pzc relative to the global pzc, and (f) ideality factor relative to the applied magnetic field. β -splines included as guides for the eye.

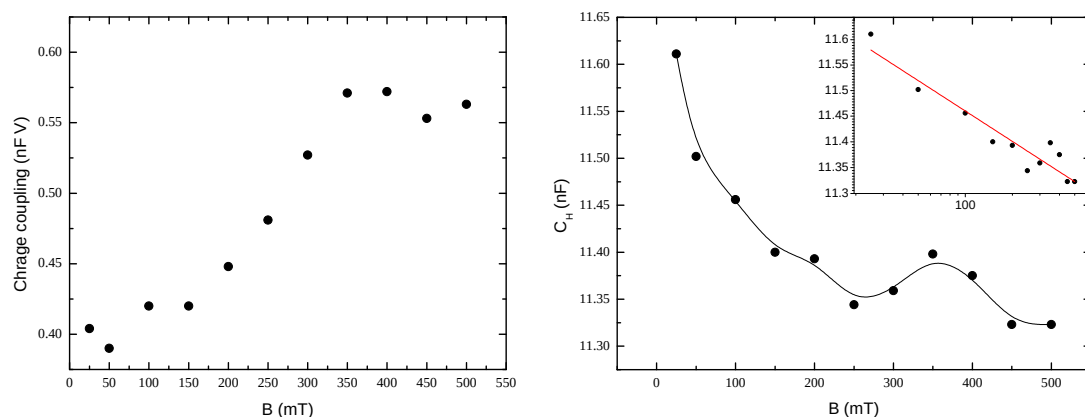


Figure 5.42: $B \parallel$ surface: (a) Potential dependent non-specific adsorption, and (b) compact layer capacitance versus applied magnetic field. β -splines included as guides for the eye.

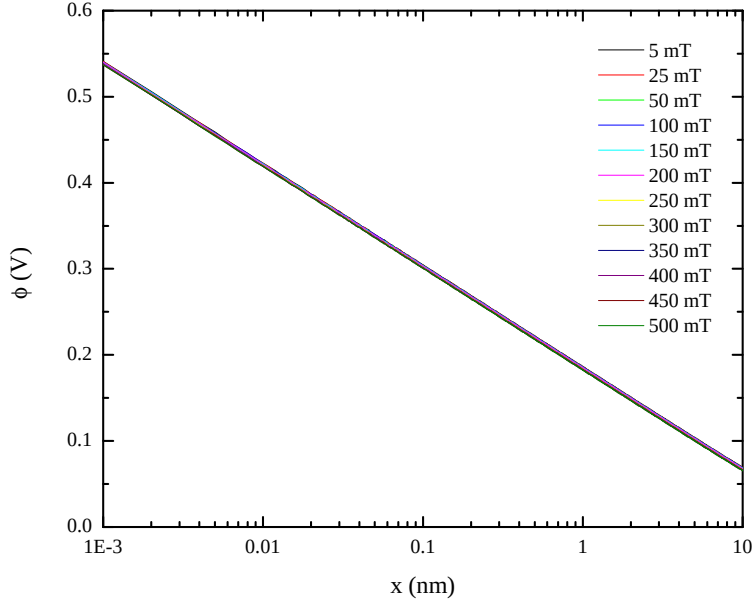


Figure 5.43: Potential profile in the double layer as a function of applied magnetic field using the $\text{NB}^{\bullet-}$ concentration values measured in the C-V curves.

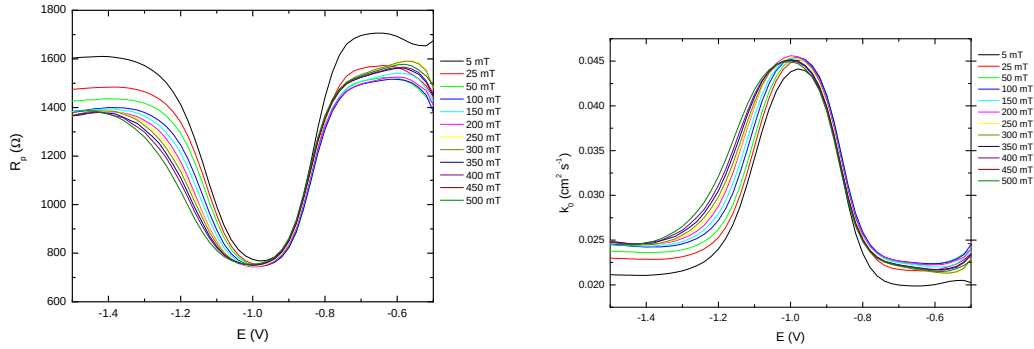


Figure 5.44: (a) Resistance-voltage curves for 0.1 M NB at 10kHz and (b) dependence of the kinetic constant with voltage and applied magnetic field.

the diffusion layer. An approximate linear dependence of the surface energy with B is observed at a range of potentials (fig. 5.50.c & d). The evolution of these slopes with electrode potential is plotted figure 5.50.e where we can observe a sharp increase in slope for negative potentials and almost no change at positive potentials. These slope values are in units of nJ T^{-1} which is a magnetic moment, which we will refer to as m_{exp} . The magnetic moment for a spin $\frac{1}{2}$ ion can be described using

$$m = \mu_B \tanh \frac{\mu_B B}{k_B T} \approx 10^{-26} \text{ J T}^{-1} \quad \text{or} \quad \text{A m}^2 \quad (5.41)$$

where μ_B is the Bohr magneton, B is the applied magnetic field, k_B is the Boltzmann

constant, and T is temperature. Assuming full coverage of the electrode by the diffusion layer, with a thickness of $200\text{ }\mu\text{m}$, the volume s

$$\text{vol} = \pi(0.25\text{ mm})^2 \cdot 0.1\text{ mm} = 2.610^{-8}\text{ l}$$

A qualitative description of the concentration of $\text{NB}^{\bullet-}$ can then be calculated from m and m_{exp} as $C_{\text{NB}^{\bullet-}} = m_{exp}/mN_a\text{ vol}$, using these assumptions and is plotted in figure 5.50.f ; *caveat lector* these calculations are only accurate to an order of magnitude. What we observe is an increase in $\text{NB}^{\bullet-}$ concentration as the potential is decreased from zero, in agreement with our knowledge that NB reduces to $\text{NB}^{\bullet-}$ at potentials less than the pzc. Qualitatively, this means as we increase the $\text{NB}^{\bullet-}$ concentration we increase the effect of the field, since we have a greater concentration of magnetic moments (fig. 5.50.e).

This is consistent with the Maxwell model, recalling that the electrostatic energy is

$$U_E = -\frac{1}{2}\sigma V = -\frac{1}{2}CV^2$$

and that a negative charge was measured at the electrode for negative voltage, and a positive charge for a positive voltage, meaning this term will retain a net negative value unless the magnetic field drives the charge to a positive value (which does not occur as seen in fig. 5.40.a). This means that the electrostatic and magnetostatic fields work in tandem, decreasing the surface tension when the magnetic field is parallel to the surface. This is a key observation that we will use to examine the perpendicular case.

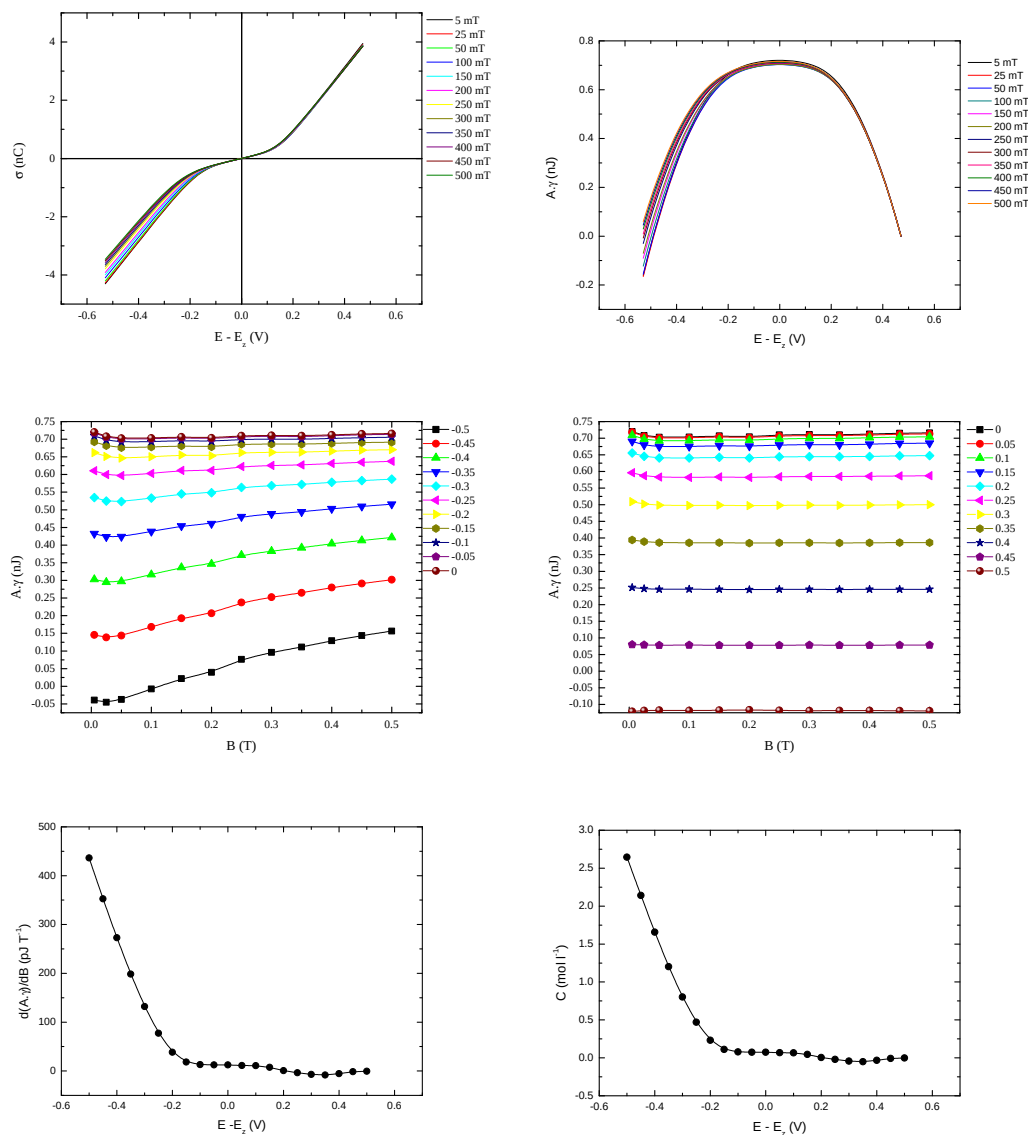


Figure 5.45: B $\parallel$ Surface: Magnetic field effects on (a) the surface charge as a function of potential, (b) the surface tension as a function of potential, (c) the surface tension for $V \leq 0$ (versus pzc) versus B, (d) the surface tension for $V \geq 0$ (versus pzc) versus B, (e) energy-field coupling (magnetic moment), and (f) effective diffusion layer $NB^{\bullet-}$ concentration as a function of V. β -splines included as guides for the eye.

When the field is perpendicular to the electrode, the high frequency impedance response is quite different to the parallel case. The double layer capacitance increases with applied magnetic field (fig. 5.46.c), indicating that the double layer thickness decreases with magnetic field, likewise the CPE ideality factor decreases towards 0.5, indicating that the surface roughness and ϕ_0 distribution becomes more important, which can only occur for a thinning double layer. Following this same trend, the charge transfer resistance increases, which we have determined depends on the position of the OHP. This series of data suggest that the magnetic field pulls ions out from the electrode surface, which is consistent with a Maxwell stress-induced oblate distortion of the diffusion layer.

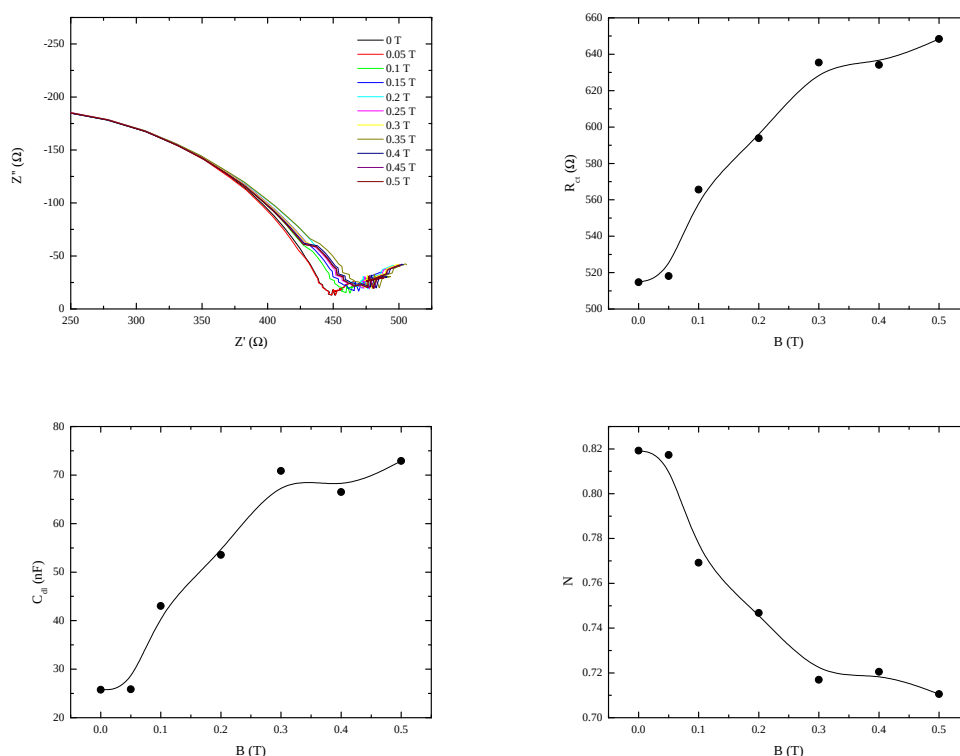


Figure 5.46: The magnetic field effect on (a) Nyquist plots of the impedance response of 0.1 M NB at the reduction potential, (b) charge transfer resistance, (c) double layer capacitance, and (d) CPE ideality factor. Note β -splines are included as guides to the eye.

Switching to capacitance-voltage curves (fig. 5.47) it is immediately noticeable that there is no obvious trend in the raw data. If instead we examine the extracted parameters from a three capacitor fit (figs. 5.48 and 5.49), it is clear that only two variables exhibit a correlation with B . First, the ideality factor for $\text{NB}^{\bullet-}$ increases from 1 to 1.3 at 0.5 T (fig. 5.48.f). This could be due to one of two things. The first possibility is that the double layer thickness has decreased (in agreement with the previous data), increasing the perturbation by the surface roughness. The other possibility is that at zero field the recombination current cancels the roughness broadening, and it is a suppression of the

recombination current that allows the broadening to occur. The former is more likely, as it is consistent with the rest of the data which all suggests that the double layer thickness decreases with applied magnetic field. Finally, the Helmholtz capacitance is seen to decrease (fig. 5.49.b), in contradiction to the other data. It is not clear if this is a magnetic field effect, or a limit in the reproducibility of the measurement. This is because the Helmholtz capacitor is more sensitive to the real surface area compared to the diffuse layer, and the working electrode must be cleaned and polished between each measurement; leading to an unmeasurable and unpredictable change in real surface area. The C_H trend could also be due to a limitation in the fitting model, as upon comparison of the experimental data and the fits, one can draw the conclusion that the fit is not optimal at the Helmholtz wings. This is most likely due to extra adsorption terms which have not been included and are outside the scope of this work to study fully. For all other parameters, no effect or clear monotonic trend is observed in the data (figs. 5.48 and 5.49). There is no clear effect on either $\text{NB}^{\bullet-}$ or TBA^+ concentration in the diffuse double layer, nor any measurable effect on their local pzcs, or the non-specific ion adsorption.

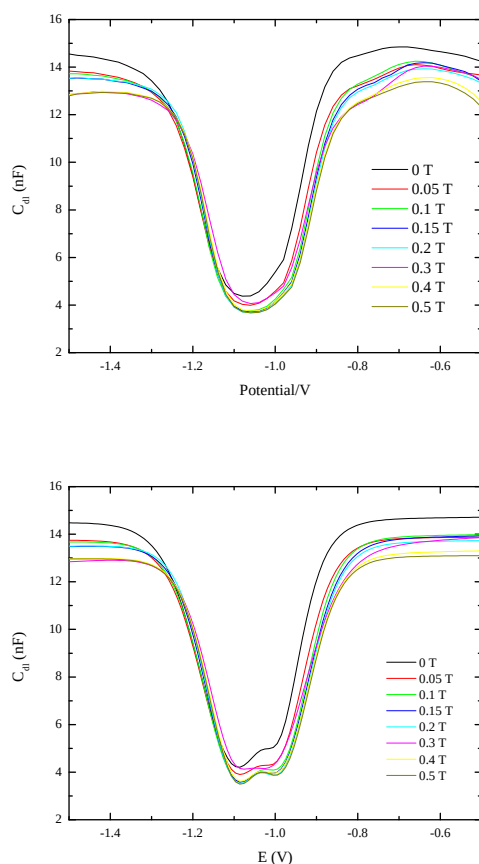


Figure 5.47: Capacitance-voltage curves for 0.1 M NB at 10kHz with B perpendicular to the surface (a) measured data and (b) theoretical fits

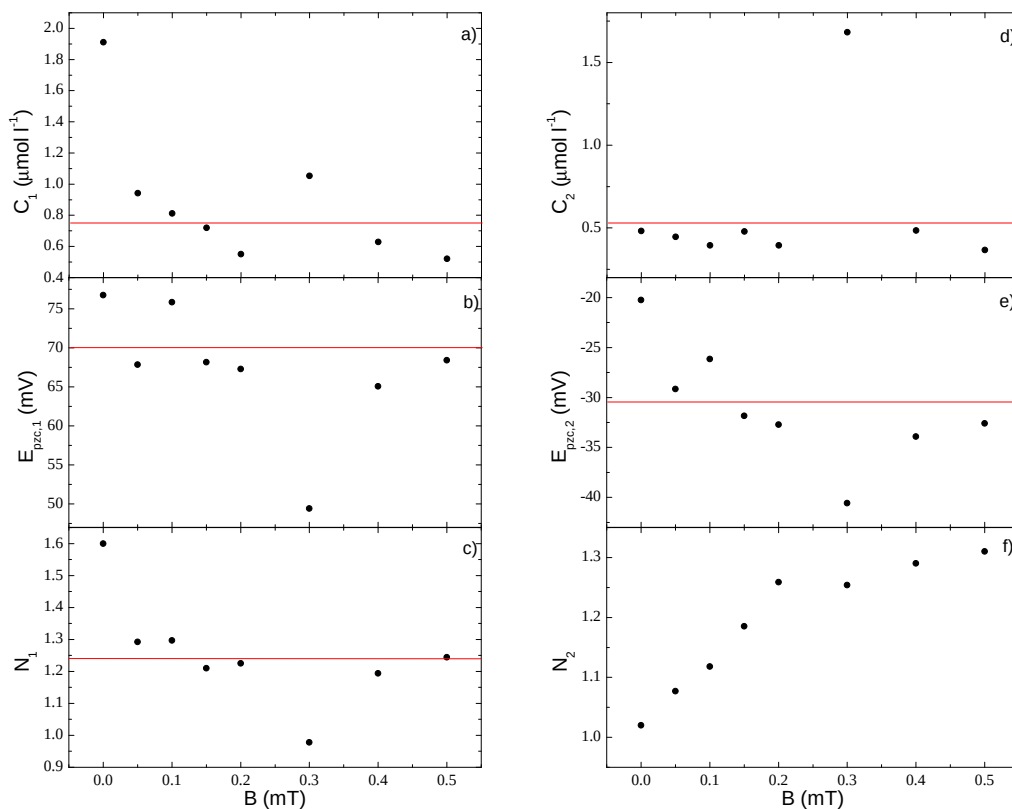


Figure 5.48: $B \perp$ surface: TBA^+ : (a) Concentration in the diffuse layer, (b) pzc relative to the global pzc, and (c) ideality factor relative to the applied magnetic field. **$\text{NB}^{\bullet-}$:** (d) concentration in the diffuse layer, (e) pzc relative to the global pzc, and (f) ideality factor relative to the applied magnetic field. β -splines included as guides for the eye.

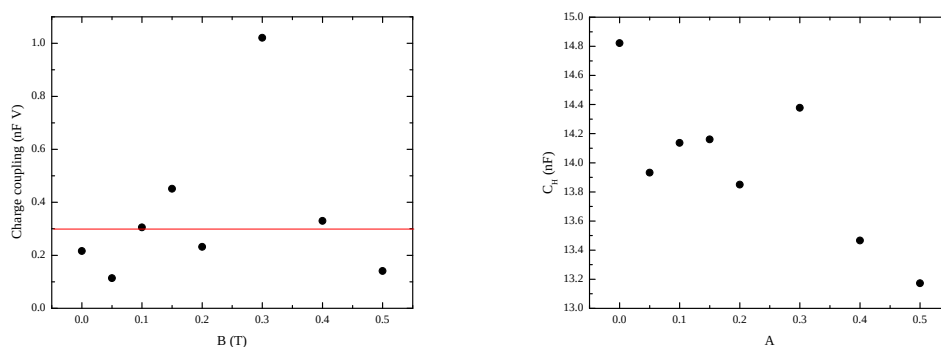


Figure 5.49: $B \perp$ surface: (a) Potential dependent non-specific adsorption, and (b) compact layer capacitance versus applied magnetic field. β -splines included as guides for the eye.

5. MAGNETOELECTROCHEMISTRY WITH MODEL SYSTEMS

Clearly this approach is not enough to give us meaningful data about the the energy interactions at the electrode surface. Next we draw our attention to the surface energy arising from the surface tension. Recalling again that the total surface energy can be described by

$$E_t = A_d\gamma_{\text{NB,Pt}} + S_{\text{NB}}\gamma_{\text{NB,SE}} - A_c\gamma_{\text{SE,Pt}} - \frac{1}{2}CV^2 - \frac{1}{2}\mu_0\chi B^2 \text{vol} \cos(2\theta)$$

We now examine the coupling of the magnetostatic and electrostatic energies, and their effect on the surface tension. In this geometry, the Maxwell stress elongates the diffusion layer perpendicular to the electrode surface (prolate). This results in a decrease in ion concentration close to the electrode surface (in agreement with the impedance spectroscopy results and capacitance - voltage data), which in turn causes a positive shift in the excess charge at the electrode surface (through the Lipmann equation 5.34).

As discussed previously, it is a fundamental limitation of the measurement system that polishing and cleaning can lead to irreproducibility in the measurements that can be difficult to prevent. Inspecting the surface energy dependence on B at a series of potentials (figs. 5.50.c & d) we observe that the surface energy decreases with magnetic field, indicating that the contact area between the $\text{NB}^{\bullet-}$ and Pt electrode has decreased, as expected if the paramagnetic phase is distorting perpendicular to the electrode surface.

This observation is illustrated in the coupling of the surface energy to the field in figure 5.50.e. As already remarked, the coupling is opposite to that of the parallel case. Here the energy decreases with magnetic field, and so close to the electrode the $\text{NB}^{\bullet-}$ is on average behaving in a quasi-diamagnetic manner; exhibited by the effective negative magnetic moment in figure 5.50.e. The magnetic field effect is smaller compared to the parallel case (fig. 5.50), and likewise is greatest in magnitude at potentials where there is a significant concentration of $\text{NB}^{\bullet-}$ at the electrode surface, fully in agreement with the Maxwell model, and all our observations.

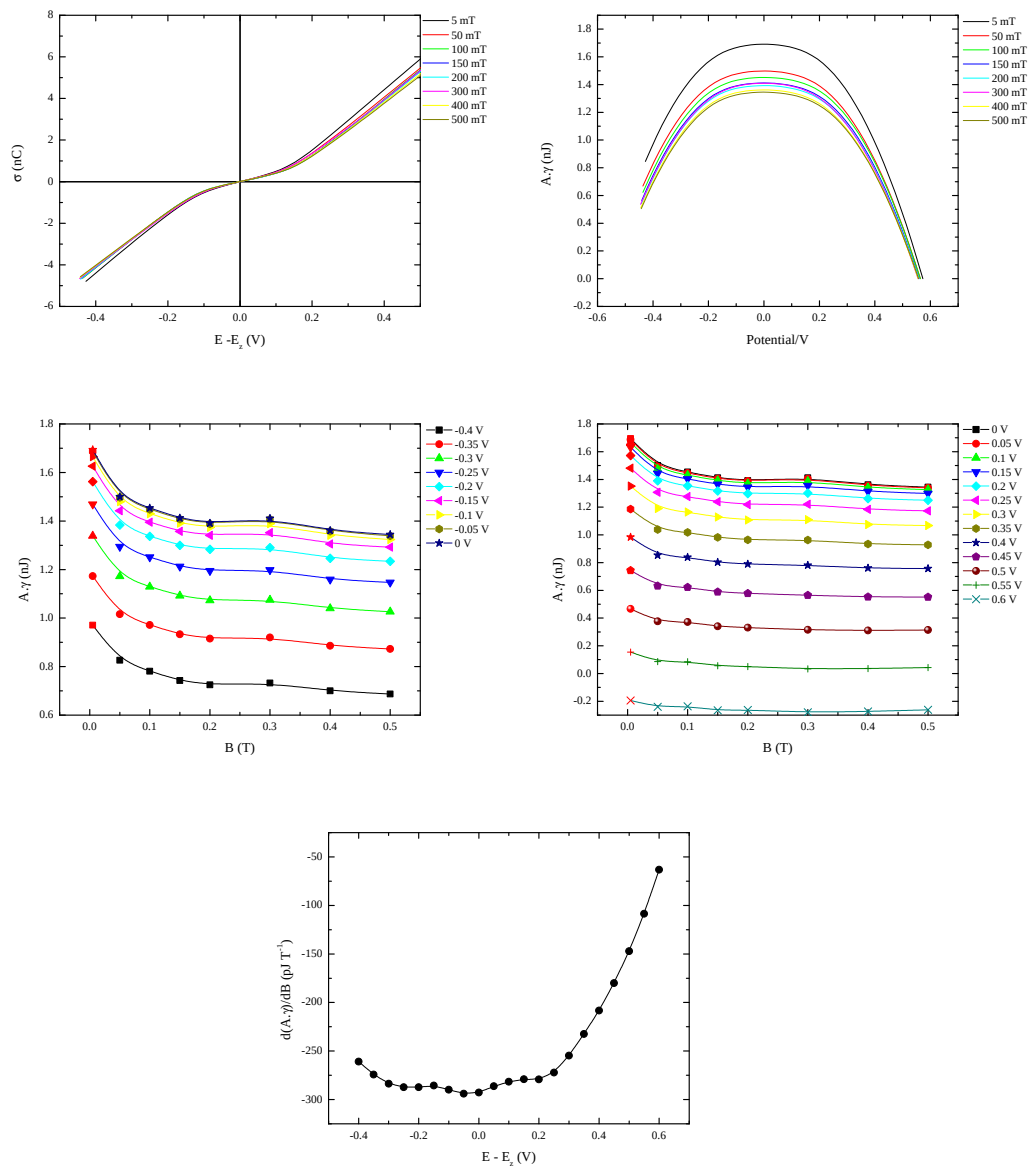


Figure 5.50: $B \parallel$ Surface: Magnetic field effects on (a) the surface charge as a function of potential, (b) the surface tension as a function of potential, (c) the surface tension for $V \leq 0$ (versus pzc) versus B , (d) the surface tension for $V \geq 0$ (versus pzc) versus B , and (e) energy-field coupling (magnetic moment). β -splines included as guides for the eye.

Finally, to gain further insight into the role of B in the measured double layer capacitance and charge transfer resistance, we return to the B parallel geometry and measure the impedance response of the cell at 10 kHz, for fixed potentials, while sweeping the field. Both the capacitance and charge transfer resistance decrease with applied magnetic field (fig. 5.52.a-d), and the response is symmetric about B; i.e. the sign of the applied field is irrelevant. As before, the response is greatest at more negative potentials where $\text{NB}^{\bullet-}$ is present in large concentration close to the electrode surface. Closer to the pzc, there is a small but measurable decrease in the capacitance, which is due to the adsorption of TBA^+ . The change in OHP potential can be related to the relative change in kinetic rate constant using the Frumkin correction

$$k^0 = k_t^0 \exp \left[\frac{(\alpha - n)F\phi_2}{RT} \right] \quad (5.42)$$

where k_t^0 is the double layer corrected true rate constant, α is the charge transfer coefficient, and F is Faraday's constant; which can be written as

$$\Delta\phi_2^{B,0} = \frac{RT}{(\alpha - z)F} \ln(k_b^0/k_0^0) \quad (5.43)$$

where $\phi_2^{B,0}$ is the OHP potential change from zero field to a magnetic field B, k_b^0 and k_0^0 are the measured kinetic constants with and without an applied magnetic field. The dramatic drop in charge transfer resistance with B corresponds to a more modest change in OHP potential (ϕ_2 , see fig. 5.52.e); approaching a negative shift of 25 mV in 0.9 T. Inspecting figure 5.40.d we can see that to achieve a shift of 25 mV at an electrode potential of $\phi_0 = -1.2$ V only requires a shift of ~ 1 Å, in agreement with the data extracted from the capacitance-voltage graphs. The strength of the coupling of $\Delta\phi_2$ to the magnetic field can give us a qualitative idea of the interaction of the magnetostatic energy on the electrostatic. At $\phi_0 = -1.2$ V, $\Delta\phi_2$ clearly exhibits three different B dependence regimes (fig. 5.51). From 0 T to ≈ 0.1 T, $\Delta\phi_2 \propto B^{2.5}$. Once the magnetic field increases further the coupling drops down to a linear relationship until a field of ≈ 0.3 T is reached, and from there onwards $\Delta\phi_2 \propto B^{0.5}$. It can be conjectured that the power law dependence of each field regime is a measure of the relative strengths of the electrostatic and magnetostatic energies. A purely magnetostatic dependence would have $\Delta\phi_2 \propto B^2$ for all magnetic fields. A low fields, the $\text{NB}^{\bullet-}$ concentration in the diffusion layer is still low, so the excess negative charge is still large, and the coupling of the charge to the magnetic field will accelerate the shift in the OHP layer. Once the concentration of $\text{NB}^{\bullet-}$ increases, we begin to reach a saturation point where the concentration is so large that the excess charge can go to zero, or even become positive at a negative potential. The suppression of surface tension by the electrostatic force essentially gets progressively weaker for higher $\text{NB}^{\bullet-}$ concentrations, leading to a linear and finally sub-linear dependence on the magnetic field. The exact coupling

between the energies has yet to be derived.

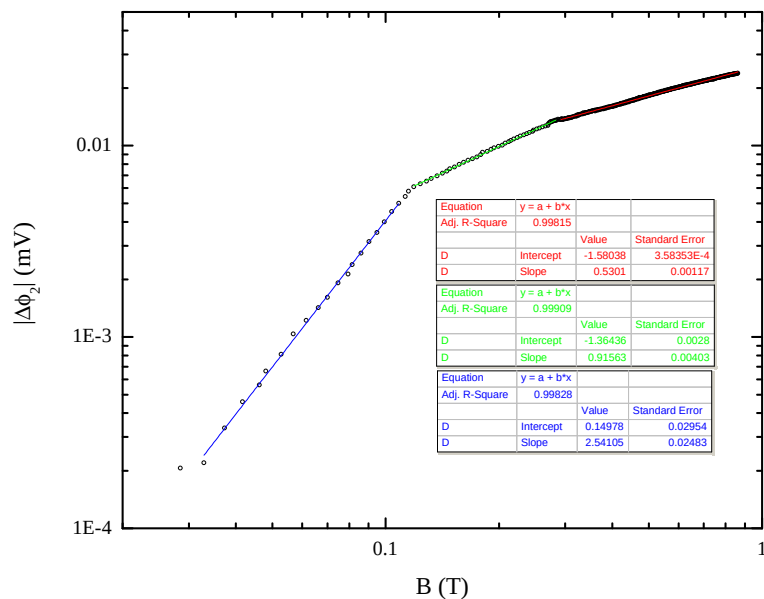


Figure 5.51: The change in OHP potential with applied magnetic field, showing three clear power law regimes with $\delta\phi_2 \propto B^{2.5}$, $\approx B^1$, and $\approx B^{0.5}$

A final validation test of the model, involves a short study of the dynamics of the distortion. Upon the application of a magnetic field, an instantaneous distortion of the $\text{NB}^{\bullet-}$ phase would not be expected, as the stress must overcome the inertia of the system. Measuring the capacitance-field curves as a function of magnetic field sweep rate should expose this inertia; giving us a qualitative description of the distortion. Even for sweep rates as low as 13 mT s^{-1} , a phase shift or delay is evident (fig 5.53.a). As the sweep rate increases so too does the peak separation, as illustrated by figure 5.53.f; showing that the Maxwell stress is a dynamic response to the change in total energy, and is not an instantaneous response. However, it is important to point out that this model dependent, and the stress is assumed to be isotropic.

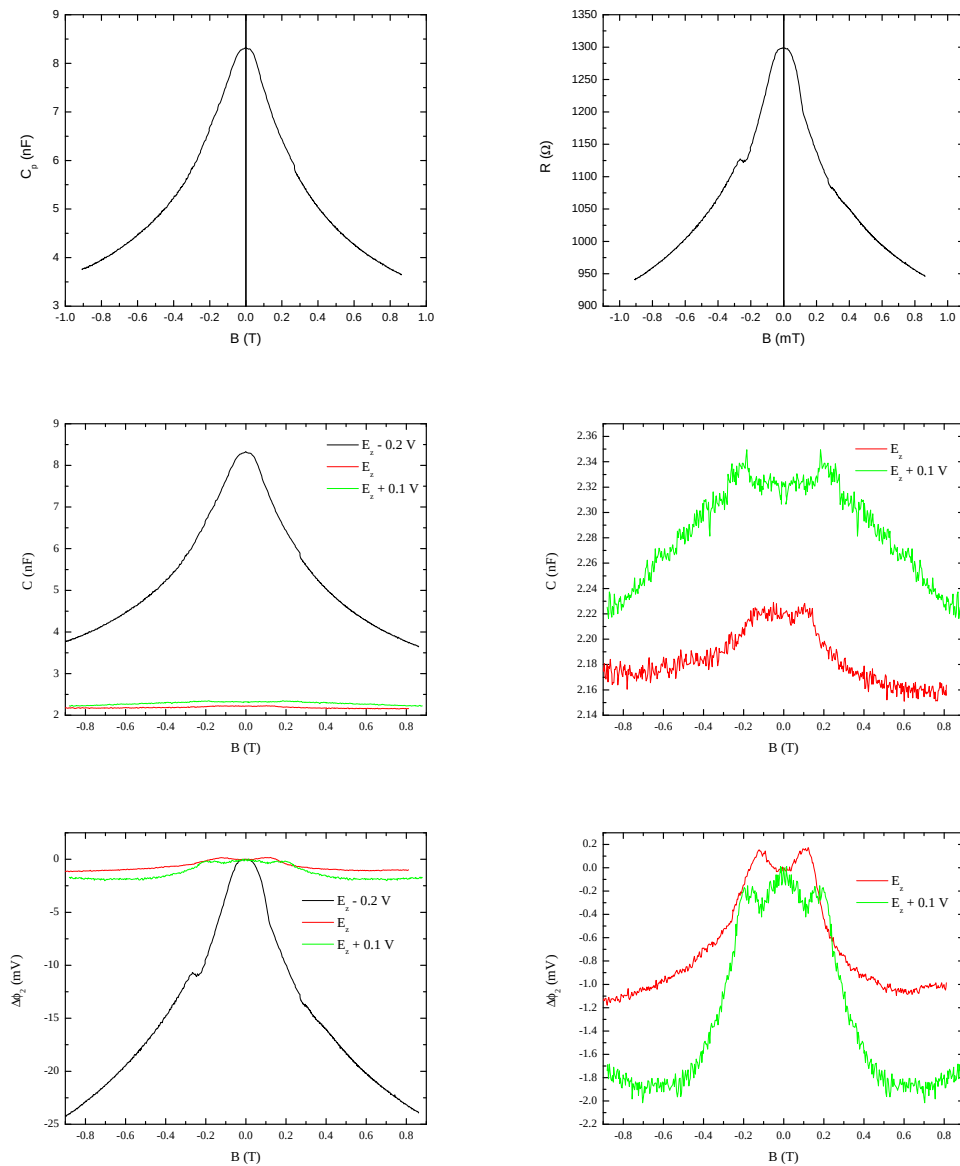


Figure 5.52: Magnetic field sweeps at $< 1 \text{ mT s}^{-1}$ (a) double layer capacitance at -1.2 V (pzc - 0.2 V), (b) charge transfer resistance at at -1.2 V (pzc - 0.2 V), (c) double layer capacitance for three potentials, (d) double layer capacitance at pzc and pzc + 0.2 V, (e) OHP potential for three potentials, and (f) OHP potential at pzc and pzc + 0.2 V

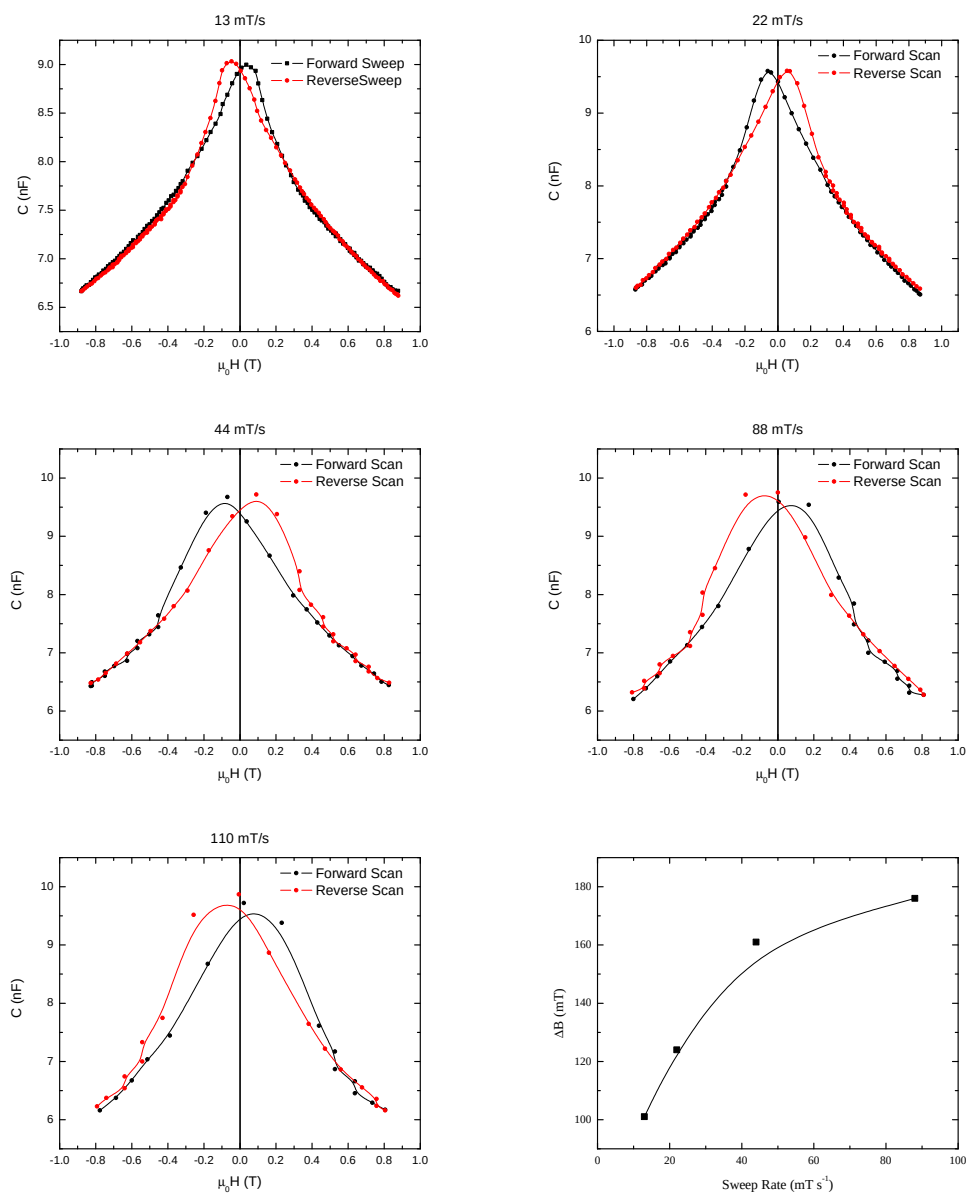


Figure 5.53: Double layer capacitance as a function of B for sweep rates of (a) 13 mT s⁻¹, (b) 22 mT s⁻¹, (c) 44 mT s⁻¹, (d) 88 mT s⁻¹, and (e) 110 mT s⁻¹; and (f) Capacitance peak separation as a function of sweep rate. β -plines included as guides for the eye.

5.2.4 Comparison Systems

Two comparison systems were chosen as null hypothesis tests. The first was the reduction of the ferricenium ion in acetonitrile, and the second was the reduction of the charge anthracene radical in acetonitrile.



20 mM solutions of both species was used, with 0.2 M TBAP supporting electrolyte in acetonitrile. Both systems are well known and well characterised mass transport limited systems in acetonitrile [1, 15–17]. In acetonitrile, ferrocene is a quasi-reversible one electron transfer system, and anthracene is an irreversible one electron transfer system. In both systems, the magnetic field was applied parallel to the electrode surface, to induced the maximum expected effect, therefore increasing the likelihood of being able to detect any effects. We have seen that a magnetic field interacts with the NB electrochemical system in two ways, and in two locations, first the Lorentz force magneto-convection acting on the diffusion layer, and second the Maxwell stress (which can include a magnetic field gradient term) acting on the double layer. Measurable magnetic field effects are predicated on having charged ions (Lorentz force) and paramagnetic species (Maxwell stress) in solution to see any effects. Here the roles are reversed from NB, which is a neutral molecule that is reduced to a paramagnetic radical. In both comparative cases the reactants are positively charged paramagnetic ions that are reduced to neutral molecules. The Maxwell stress model assumes that there will be a negligible effect of the stress on the double layer capacitance and charge transfer resistance.

5.2.4.1 Cyclic Voltammograms

Cyclic voltammograms were carried out at 100 mV s⁻¹ with the field perpendicular and parallel to the nominal current. For ferrocene/ferricenium (see fig. 5.54), while the total current in the perpendicular increases, this is all due to the background current, which when subtracted gives the results as shown in figure 5.54.c-f. No effects were seen on the oxidation currents for either B perpendicular or parallel, the only observable effect on the reduction current is with the field perpendicular. When the field is parallel, a stagnant region forms where the Lorentz force cannot act on the produced neutral species.

Similar to ferrocene, the anthracene oxidation current is unaffected by the magnetic field in the parallel configuration; however when the field is applied perpendicular to the current, the magneto-convection enhances the current and a power-law dependence on B is observed.

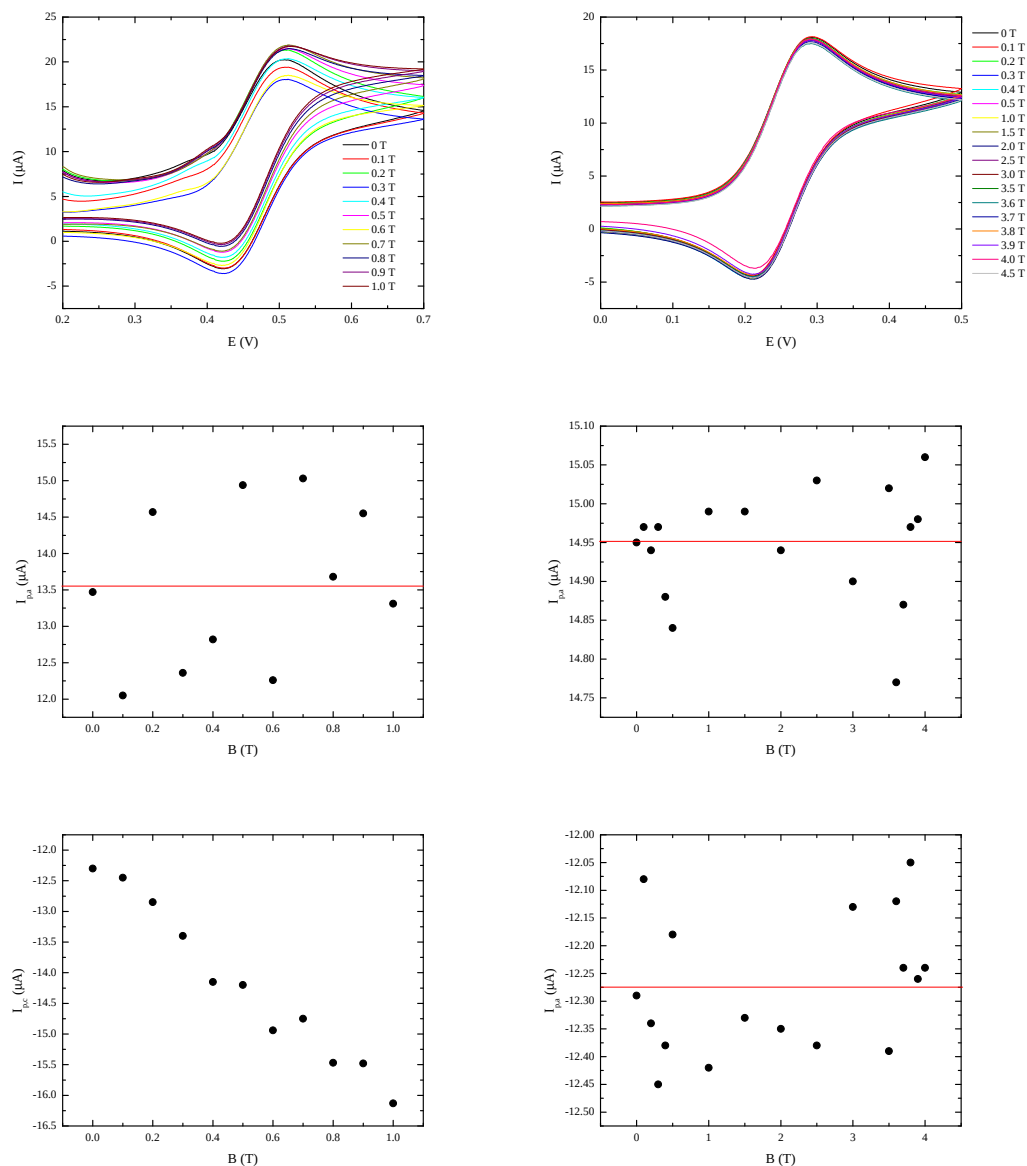


Figure 5.54: 20 mM Ferrocene: Cyclic voltammograms at 100 mV s⁻¹ with (a) B perpendicular to the current and (b) B parallel to the current; oxidation peak currents with (c) B perpendicular, and (d) B parallel; reduction peak currents with (e) B perpendicular, and (f) B parallel

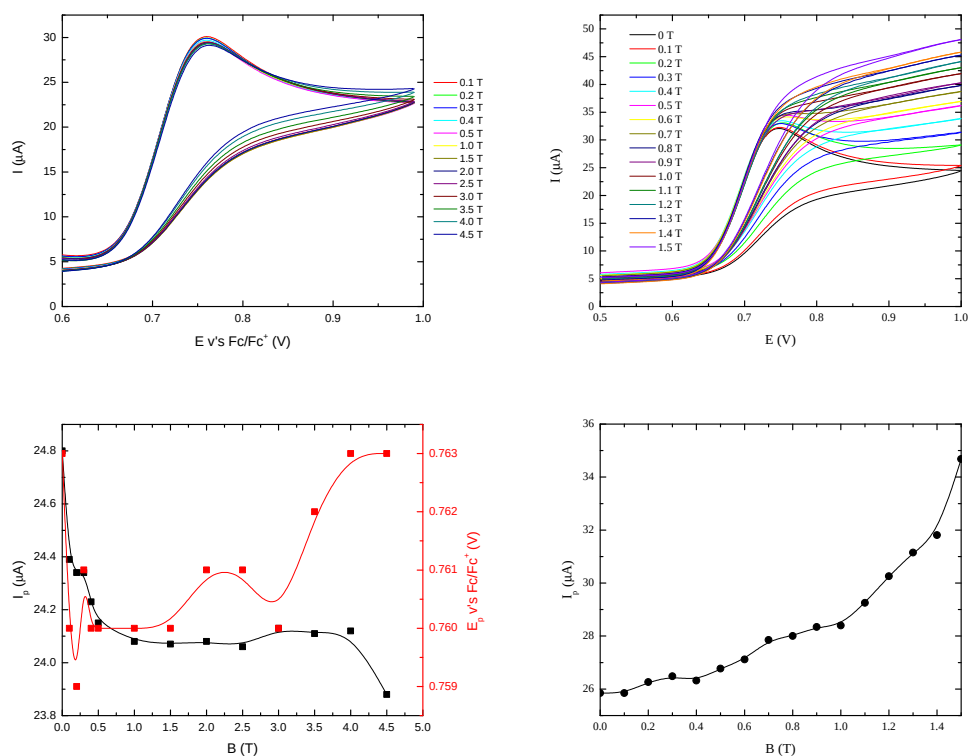


Figure 5.55: 20 mM Anthracene: Cyclic voltammograms at 100 mV s^{-1} with (a) B perpendicular to the current and (b) B parallel to the current; oxidation peak currents with (c) B perpendicular, and (d) B parallel. β -splines included as guides for the eye.

5.2.4.2 Impedance Measurements

Focusing our attention on the impedance response of the two systems, capacitance-voltage curves were measured for both systems at 5 kHz for ferrocene (fig. 5.56) and 3 kHz for anthracene (fig. 5.57). In both cases, no effect was observed on the diffuse double layer, and compact layer within the reproducibility of the measurements. Supporting the hypothesis that paramagnetic species are required to see a Maxwell stress-type effect in the double layer.

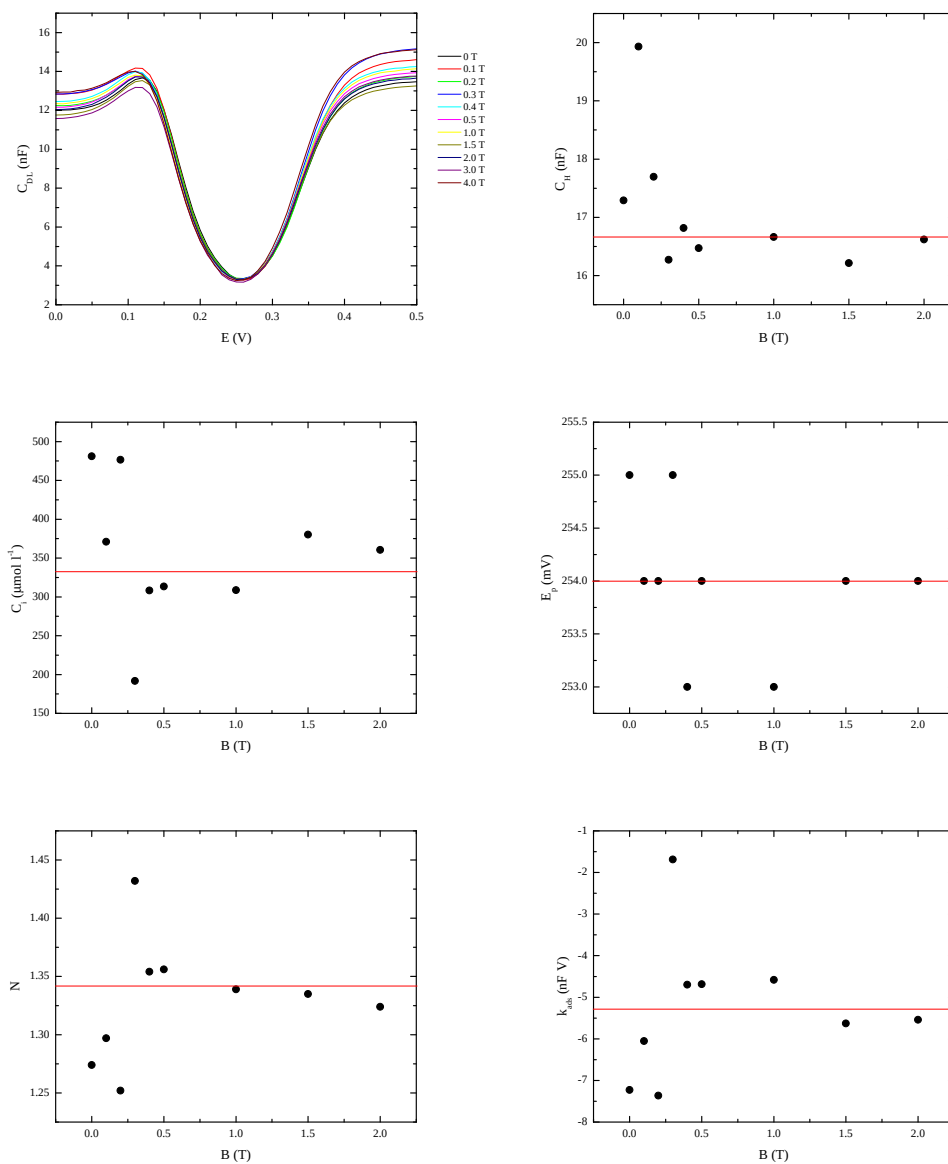


Figure 5.56: 20 mM Ferrocene: Magnetic field effects on (a) capacitance-voltage curves at 5 kHz, (b) compact layer capacitance, (c) ion concentration in the diffuse layer, (d) the pzc, (e) ideality factor, and (f) voltage dependent non-specific adsorption.

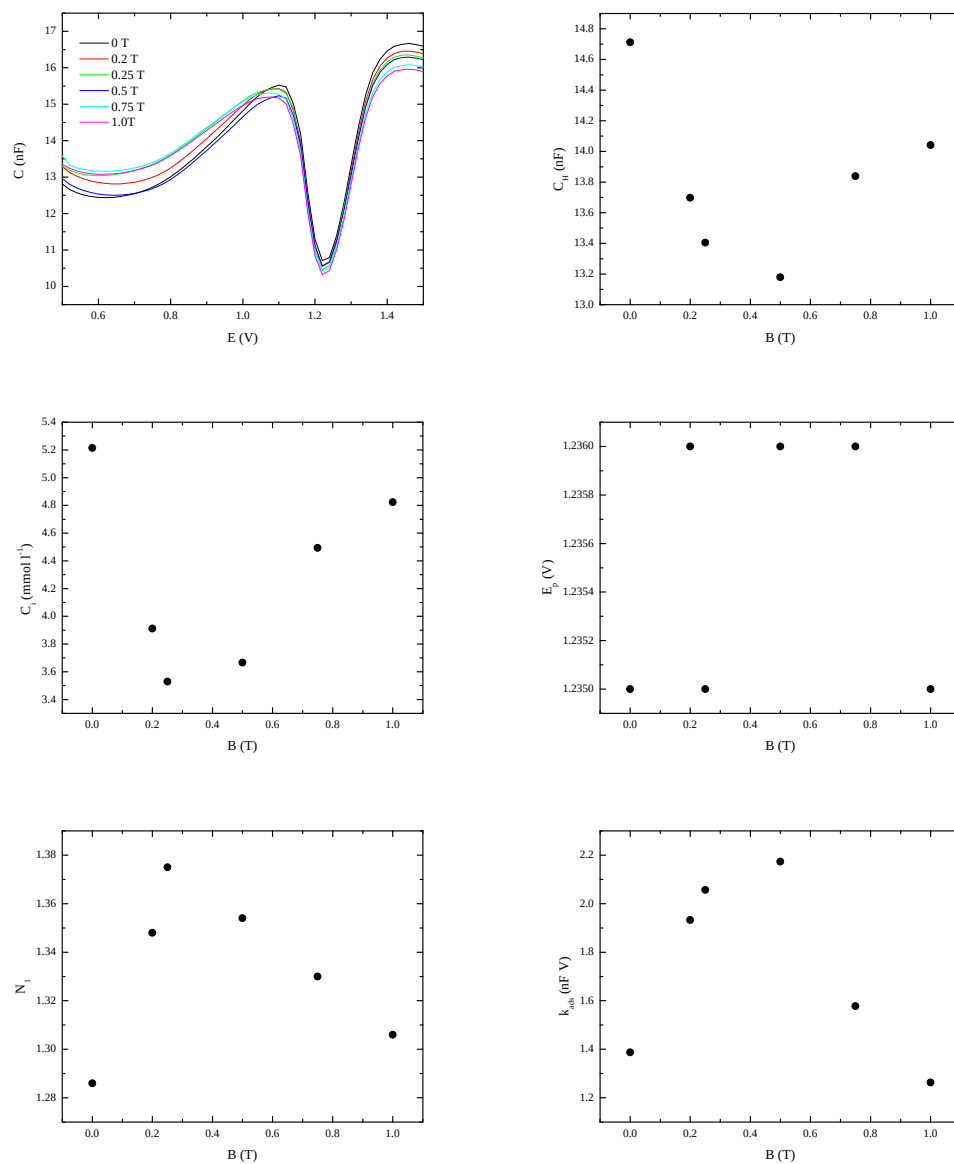


Figure 5.57: 20 mM Anthracene: Magnetic field effects on (a) capacitance-voltage curves at 5 kHz, (b) compact layer capacitance, (c) ion concentration in the diffuse layer, (d) the pzc, (e) ideality factor, and (f) voltage dependent non-specific adsorption.

5.3 Conclusions

To observe magnetic field effects in electrochemistry, the species of interest must have a charge, or be paramagnetic. If the reactants or products are charged, and the reaction is mass-transport limited, then the Lorentz force will induce magneto-convection, thinning the diffusion layer and enhancing the limiting current. For nitrobenzene, there is a clear angular dependence on Lorentz force stirring, between the current and field. The greatest current enhancement is when the nominal current and magnetic field are perpendicular. However, it is possible to observe edge effects when the field parallel, creating a vortex at the electrode surface, even though it is in an apparently zero Lorentz force configuration. Closer to the electrode, in the double layer a 3 capacitor model was used to model the double layer capacitance. The Maxwell stress was introduced to explain the increase in concentration of the $\text{NB}^{\bullet-}$ phase close to the electrode surface, even though it experiences no *net* force. The Maxwell stress lowers the surface tension at the metal/solution interface, which couples with the electrostatic forces in a complex way. The stress may be viewed as fictitious magnetic charges, which experience a force $\mathbf{f} = \mu q_m \mathbf{H}$, which repulse each other, distorting the diffusion layer to minimise its energy. This model is able to account for the numerous phenomena observed in the double layer; namely the negative shifting of the pzc with applied magnetic field, an increase in adsorption, the decrease in capacitance and charge transfer resistance, and the shifting the OHP layer closer to the electrode surface and a shift the OHP potential to more negative values. All these effects can be attributed to the Maxwell stress lowering the surface tension of the reduced paramagnetic phase in the diffuse double layer, thereby increasing the ion concentration and adsorption, and via the Lipmann equation, lowering the charge and capacitance. The greatest effects were observed at potentials where NB was actively reduced, and for an applied field parallel to the electrode surface. No effect is expected for diamagnetic ions, as is observed with ferrocene and anthracene. The observed lowering of charge transfer resistance is due to the attraction of ions to the surface by the stress, and so the ions experience a larger potential than without a magnetic field. While the change in OHP distance with field is almost negligible ($\sim 1\text{\AA}$), because the potential gradient is very steep in the double layer, this is enough to shift the OHP potential by up to -25 mV, thereby increasing the rate constant by 46%. No effect was observed on the true kinetics of the system, nor there was a net concentration gradient force measured.

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Chapter 6

Conclusions & Future Work

6.1 Conclusions

A systematic study of the magnetic field effects during the deposition and corrosion of metals in uniform and patterned magnetic fields and the reduction and oxidation of organic molecules has been carried out. In mass transport limited systems, the Lorentz force can induce convection cells down to the micron scale and enhance the limiting current of metal corrosion, which is indifferent to the magnetic properties of the electrode (chapter 3). It can also influence the balance of the hydrogen evolution reaction to Cu deposition through induced magneto-convection. The question remains, can this simple model capture the essence of all the magnetic interactions in deposition above the permanent magnet arrays, and can it be used to explain the morphology of the metal patterns deposited above the permanent magnet arrays? We already know from chapter 4 that any magnetic effects on the deposition of Cu and Co above arrays must be in the double layer. The magnetic field effect is indifferent to the bulk solution susceptibility, rather it is the interfacial susceptibility in the double layer that is important as shown by the use of bulk paramagnetic, diamagnetic and zero susceptibility solutions.

In all three cases the dot morphology followed $|\mathbf{B}|$, not ∇B or ∇B^2 as one would expect for a field gradient type force (see fig. 6.1). The Lorentz force was also ruled out by the Cu dot studies, where we saw no difference in the current for parallel and anti-parallel arrangements of magnets. However, we do know that the total energy of the system increases in a magnetic field, and recalling that the force on a magnetic charge is $\mathbf{f} = \mu q_m \mathbf{H}$, we can see that the Maxwell stress will scale with $\mathbf{H}$, and the total stress is independent of the sign of the applied field (fig. 6.2).

The only difference between $+\mathbf{H}$ and $-\mathbf{H}$ configurations is that the image charges will swap position, i.e. the magnetisation direction reverses, but the total stress remains the same. The energy of a Cu^{2+} or Co^{2+} ion in a 1 T field is between 2 and three orders of magnitude greater than that for $\text{NB}^{\bullet-}$, therefore it is quite likely that the shift in OHP potential could be even greater. Therefore encouraging preferential growth sites

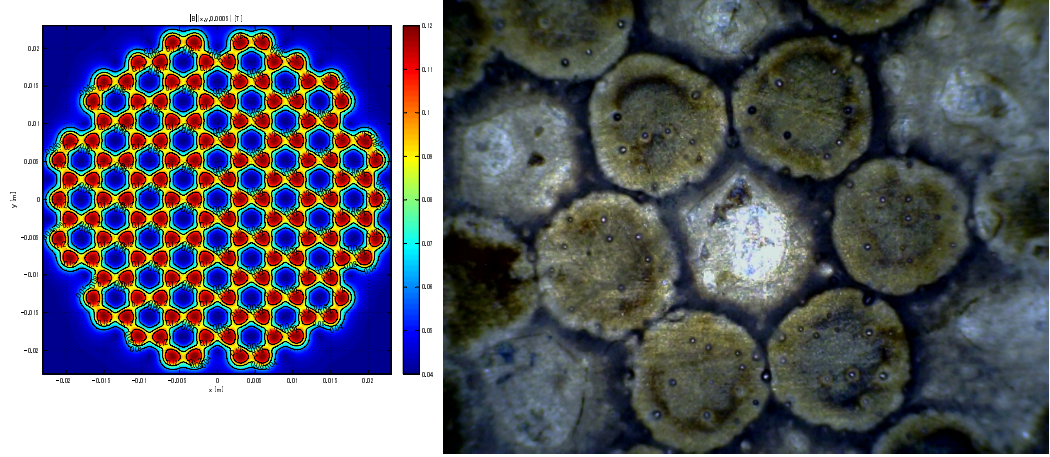


Figure 6.1: Array 6, ‘HD’, hexagonal lattice, diagonal line alternating: (a) $|B|$ at $z = 0.5$ mm, (b) shape of Co deposit above ‘HD’ array, and (c) shape of inverse Cu deposit from concentrated $\text{Dy}(\text{NO}_3)_3$ solution.

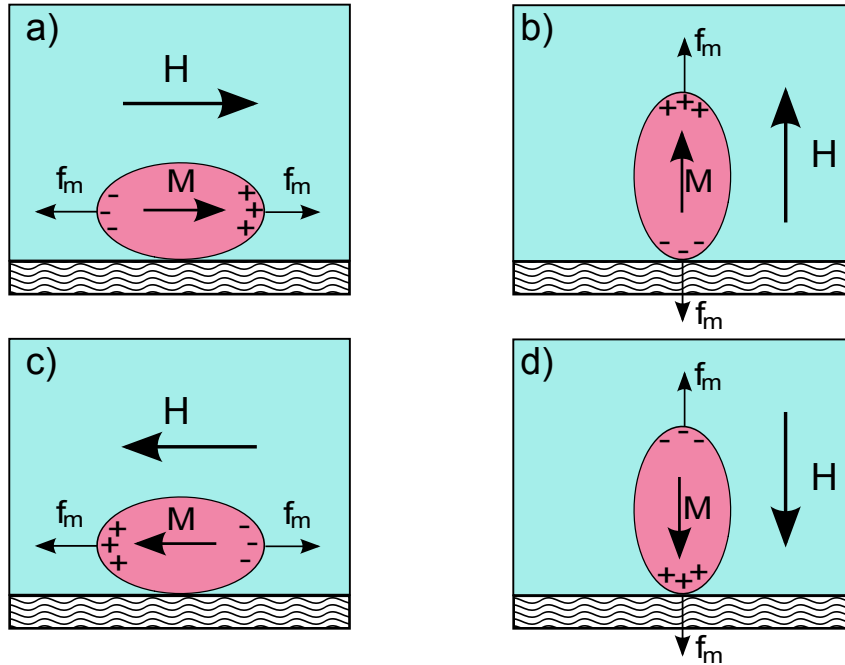


Figure 6.2: The deformation of a net paramagnetic liquid at an electrode surface due to Maxwell stresses. (a) & (c) show the case when the magnetostatic forces are greater than those from the electrostatic field in the z -direction, (b) & (d) show the case when the magnetostatic forces are less than the electrostatic forces in the z -direction.

during the early deposition period. This is what is observed for weakly paramagnetic Cu^{2+} ions; during potentiostatic deposition there is only an effect on the initial current, and *not* on the limiting current. The decrease in surface tension can also explain why the Dy^{3+} ions in the concentrated $\text{Dy}(\text{NO}_3)_3$ solution suppress Cu deposition above the regions of high magnetic field. The Dy^{3+} ions will experience strong Maxwell stress, attracting the ions much closer to the electrode surface than the Cu^{2+} ions, thus lowering the effective potential experienced by the majority of copper ions as they are forced further away from the electrode surface. It is also this effective increase in kinetic rate constant that allows the DyO_x deposits to form above magnetic fields. Therefore this is a promising route to explore, endeavouring to lower the energy barrier, and potentials required to deposit Dy in conventional electrochemical cells.

Finally, electrodeposition using magnetic templates and inverse templates has been demonstrated down to micron scales. The nitrobenzene data supports the hypothesis that the origin of the effect is the Maxwell stress, or magneto-static energy on the depositing ions in the diffuse double layer. The benefit of this templating method is that since the stress scales with B , lateral dimensions of any structures is only limited by the lateral geometry of the magnetic template; however it is crucial to get the template as close to the depositing surface as possible since the magnetic field drops off as z^{-3} .

6.2 Future Work

6.2.1 Fundamentals

There are still a number of questions arising from the Maxwell stress model developed herein. First how do the magnetostatic and electrostatic energies interact. The exact reason for the multi-regime dependence of the OHP potential on the applied magnetic field is still unknown as it depends on the previously mentioned coupling. It also remains to be seen if these effects can be observed during metal deposition.

6.2.2 Applications

The magnetic templating introduced and prototyped in chapter 4 needs to be developed further, to optimise the deposit morphology, and to see if it is possible to scale the effect down to nanometer dimensions. Patterened magnetic arrays can also find applications in electrochemical sensors, where increased sensitivity might be possible with correctly designed structures. Finally coated ferromagnetic nanoparticle/nanowire electrodes can also be designed to improve the efficiency of batteries/fuel cells, in both the kinetic regime with the Maxwell stress, and the mass transport limited regime with the Lorentz force.

Appendix A

Derivation of Helmholtz Force

The response of a paramagnetic liquid in an external magnetic field can be described by a force density, or a surface stress, related by

$$\int f_i dV = \oint \sigma_{ik} dA_k \quad (\text{A.1})$$

where f_i is the i^{th} component of the force *density*, σ_{ik} is the stress tensor, and $\sigma_{ik} df_k = \sigma_{ik} n_k dA$ is the i^{th} component of the force on a surface element dA_k (n_k is the k^{th} component of the outward unit vector, $\mathbf{n}$, normal to the surface). By Gauss' theorem (A.24a) becomes $\int f_i dV = \int \nabla \cdot \sigma_{\mathbf{i}\mathbf{k}} dV = \int (\partial \sigma_{ik} / \partial x_k) dV$. Since the volume is arbitrary this simplifies to

$$f_i = \frac{\partial \sigma_{ik}}{\partial x_k} \quad (\text{A.2})$$

To calculate the stress tensor, we treat an infinitesimally small surface element, dA , as a planar structure of thickness h sandwiched between two planar, parallel and magnetically transparent material with $\mu \approx \mu_0$ (see fig.), all in an external magnetic field $\mathbf{H}$. Thus the force can be determined via the creation of virtual work by an arbitrary and infinitesimal displacement of the upper plate through a vector ξ . The per unit area force on the surface is $-\sigma_{ik} n_k$, the work done by the virtual displacement is $-\sigma_{ik} n_k \xi_i$, and we assume an isothermal, homogeneous deformation of the paramagnetic medium.

Next we introduce some important thermodynamic relations and a recasting of the total energy U and the free energy F with $\mathbf{H}$ and $\mathbf{B}$ as the independent variables. The change in total energy density of the system in the presence of a magnetic field is

$$dU = T dS + \zeta d\rho + \mathbf{B} \cdot d\mathbf{H} \quad (\text{A.3})$$

where U is the internal, or total energy per unit volume, T is the temperature, S is the entropy per unit volume, ζ is the chemical potential, ρ is the liquid density, and $\mathbf{H} \cdot \mathbf{B}$ is the work done per unit volume in the external magnetic field. From the relation of the free energy density $F = U - TS$ (F , U , and S are denoted here as being per unit

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volume), we can now write the change in free energy density as

$$dF = -S dT + \zeta d\rho + \mathbf{B} \cdot d\mathbf{H} \quad (\text{A.4})$$

We define the thermodynamic potentials as

$$\tilde{U} = U - \mathbf{B} \cdot \mathbf{H} \quad (\text{A.5})$$

$$\tilde{F} = F - \mathbf{B} \cdot \mathbf{H} \quad (\text{A.6})$$

and the change in potentials, while assuming a linear medium ($\mathbf{B} = \mu\mathbf{H}$) become

$$d\tilde{U} = T dS + \zeta d\rho - \mu\mathbf{H} \cdot d\mathbf{H} \quad (\text{A.7})$$

$$d\tilde{F} = -S dT + \zeta d\rho - \mu\mathbf{H} \cdot d\mathbf{H} \quad (\text{A.8})$$

Integration of (A.7) and (A.12) leads to

$$\tilde{U} = U_0(S, \rho) - \frac{\mu H^2}{2} \quad (\text{A.9})$$

$$\tilde{F} = F_0(T, \rho) - \frac{\mu H^2}{2} \quad (\text{A.10})$$

where U_0 and F_0 are the energies in the absence of an external magnetic field.

Returning to our paramagnetic surface element, the external magnetic field $\mathbf{H}$ induces fictitious magnet charges at its upper and lower boundaries, analogous to a dielectric in a planar capacitor, generating a magnetic potential ϕ_m ; related to $\mathbf{H}$ by $\mathbf{H} = -\nabla\phi_m$. To treat the magnetic field as the gradient of a scalar potential there must be no currents flowing in the system; as can be seen from the following relation

$$\mathbf{J} = \nabla \times \mathbf{H} = -\nabla \times \nabla\phi_m \equiv 0$$

The work done in an isothermal deformation at constant magnetic potential from is equal to the decrease of the free energy $\int \tilde{F} dV$, which is $h\tilde{F}$ per unit surface area. Thus the work done is

$$\sigma_{ik}\xi_i n_k = \delta(h\tilde{F}) = h\delta\tilde{F} + \tilde{F}\delta h \quad (\text{A.11})$$

At fixed temperature and magnetic field, deformations which do not change the density of the fluid (shear stresses) have no influence on the thermodynamic state, thus the variation of $\delta\tilde{F}$ in our isothermal deformation, recalling (A.12) is

$$\begin{aligned} \delta\tilde{F} &= \left(\frac{\partial\tilde{F}}{\partial\mathbf{H}} \right)_{T,\rho} \cdot \delta\mathbf{H} + \left(\frac{\partial\tilde{F}}{\partial\rho} \right)_{\mathbf{H},T} \delta\rho \\ &= -\mathbf{B} \cdot \delta\mathbf{H} + \left(\frac{\partial\tilde{F}}{\partial\rho} \right)_{\mathbf{H},T} \delta\rho \end{aligned} \quad (\text{A.12})$$

The change in the density of the layer is related to the change in its thickness by

$$\delta\rho = -\rho\frac{\delta h}{h} \quad (\text{A.13})$$

At a point $\mathbf{r}$, after the deformation, we have matter that was at $\mathbf{r} - \mathbf{u}$, where $\mathbf{u}$ is the particle displacement vector. Under the conditions of homogeneous deformation and constant magnetic potential at the interfaces, each particle carries its own magnetic potential with it. Therefore the change in magnetic potential at a given point in space is

$$\begin{aligned} \delta\phi_m &= \phi_m(\mathbf{r} - \mathbf{u}) - \phi_m(\mathbf{r}) = \mathbf{u} \cdot \left(\frac{\phi_m(\mathbf{r}) - \phi_m(\mathbf{r} - \mathbf{u})}{\mathbf{u}} \right) \\ &= -\mathbf{u} \cdot \nabla\phi_m = \mathbf{u} \cdot \mathbf{H} \end{aligned} \quad (\text{A.14})$$

Since this is a uniform deformation,

$$\mathbf{u} = \frac{z\xi}{h} \quad (\text{A.15})$$

where z is the distance from the lower plate. Therefore the variation of the field is

$$\delta\mathbf{H} = -\mathbf{n}\frac{(\mathbf{H} \cdot \xi)}{h} \quad (\text{A.16})$$

Substituting (A.16) into (A.12) while noting that $\delta h = \xi_x = \xi \cdot \mathbf{n}$ we derive the following:

$$\begin{aligned} \delta\tilde{F} &= -\mathbf{B} \cdot -\mathbf{n}\frac{(\mathbf{H} \cdot \xi)}{h} + \left(\frac{\partial\tilde{F}}{\partial\rho} \right)_{\mathbf{H},T} \delta\rho \\ &= \frac{(\mathbf{n} \cdot \mathbf{B})(\mathbf{H} \cdot \xi)}{h} - \frac{\rho}{h}(\xi \cdot \mathbf{n}) \left(\frac{\partial\tilde{F}}{\partial\rho} \right)_{\mathbf{H},T} \end{aligned} \quad (\text{A.17})$$

Next we substitute (A.17) into the work done (A.17):

$$\sigma_{ik}n_k\xi_i = h \cdot \frac{(\mathbf{n} \cdot \mathbf{B})(\mathbf{H} \cdot \xi)}{h} - h \cdot \frac{\rho}{h}(\xi \cdot \mathbf{n}) \left(\frac{\partial\tilde{F}}{\partial\rho} \right)_{\mathbf{H},T} + \tilde{F}\delta h \quad (\text{A.18a})$$

$$= (\mathbf{n} \cdot \mathbf{B})(\mathbf{H} \cdot \xi) - \rho(\xi \cdot \mathbf{n}) \left(\frac{\partial\tilde{F}}{\partial\rho} \right)_{\mathbf{H},T} + \tilde{F}(\xi \cdot \mathbf{n}) \quad (\text{A.18b})$$

$$= n_k B_k H_i \xi_i - \xi_i n_k \rho \left(\frac{\partial\tilde{F}}{\partial\rho} \right)_{\mathbf{H},T} \delta_{ik} + \xi_i n_k \tilde{F} \delta_{ik} \quad (\text{A.18c})$$

$$= \xi_i n_k \left[\tilde{F} - \rho \left(\frac{\partial\tilde{F}}{\partial\rho} \right)_{\mathbf{H},T} \delta_{ik} + \tilde{F} \delta_{ik} \right] \quad (\text{A.18d})$$

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where δ_{ik} is the Kronecker delta. Thus, dividing by $\xi_i n_k$, the stress tensor is

$$\sigma_{ik} = \left[\tilde{F} - \rho \left(\frac{\partial \tilde{F}}{\partial \rho} \right)_{\mathbf{H}, T} \right] \delta_{ik} + H_i B_i \quad (\text{A.19})$$

Assuming a linear, isotropic medium, two further simplifications can be made, (a) $\mathbf{H} \parallel \mathbf{B}$, or $H_i B_i = H_k B_i$, and $\mathbf{B} = \mu \mathbf{H}$, then

$$\tilde{F} = F_0(\rho, T) - \frac{\mu H^2}{2} \quad (\text{A.20})$$

where F_0 is the free energy per unit volume without an external magnetic field. A well known thermodynamic relation is that the partial derivative of the free energy per unit mass with respect to volume at constant temperature is a pressure

$$\left(\frac{\partial F}{\partial V} \right)_T = -P \quad \text{or} \quad (\text{A.21a})$$

$$\left[\frac{\partial}{\partial(1/\rho)} \left(\frac{F_0}{\rho} \right) \right]_T = F_0 - \rho \left(\frac{\partial F_0}{\partial \rho} \right)_T = -P_0 \quad (\text{A.21b})$$

Substituting (A.21b) into (A.18d) leads to

$$\sigma_{ik} = \left[F_0(\rho, T) - \frac{\mu H^2}{2} - \rho \left(\frac{\partial F_0}{\partial \rho} \right)_T + \frac{H^2 \rho}{2} \left(\frac{\partial \mu}{\partial \rho} \right)_T \right] \delta_{ik} + \mu H_i H_k \quad (\text{A.22a})$$

$$\sigma_{ik} = -P_0(\rho, T) \delta_{ik} - \frac{H^2}{2} \left[\mu - \rho \left(\frac{\partial \mu}{\partial \rho} \right)_T \right] \delta_{ik} + \mu H_i H_k \quad (\text{A.22b})$$

The force acting on the paramagnetic liquid using

$$\mathbf{f} = \nabla \sigma_{ik} \quad (\text{A.23})$$

is thus

$$f_i = \partial \sigma_{ik} / \partial x_k = \frac{\partial}{\partial x_i} \left[-P_0 + \frac{H^2}{2} \rho \left(\frac{\partial \mu}{\partial \rho} \right)_T \right] - \frac{H^2}{2} \frac{\partial \mu}{\partial x_i} \quad (\text{A.24a})$$

$$- \frac{\mu}{2} \frac{\partial H^2}{\partial x_i} + B_k \frac{\partial H_i}{\partial x_k} + H_i \frac{\partial B_k}{\partial x_k} \quad (\text{A.24b})$$

$$(\text{A.24c})$$

but $\nabla \cdot \mathbf{B} = \nabla \cdot \mathbf{H} = 0$, i.e. $H_i \partial B_k / \partial x_k = 0$, therefore

$$f_i = \frac{\partial}{\partial x_i} \left[-P_0 + \frac{H^2}{2} \rho \left(\frac{\partial \mu}{\partial \rho} \right)_T \right] - \frac{H^2}{2} \frac{\partial \mu}{\partial x_i} - B_k \left(\frac{\partial H_i}{\partial x_k} - \frac{\partial B_k}{\partial x_i} \right) \quad (\text{A.25})$$

However, we assumed there are no currents in the system, therefore $\nabla \times \mathbf{H} = 0$, thus the final term on the right hand side is zero. Finally, to relate the force density to the

susceptibility we remember that

$$\mu = \mu_0(1 + \chi) \quad (\text{A.26})$$

where μ_0 is the permeability of free space, and χ is the susceptibility of the material. Thus

$$\frac{\partial \mu}{\partial x_i} = \mu_0 \frac{\partial}{\partial x_i} [1 + \chi] = \mu_0 \frac{\partial \chi}{\partial x_i}. \quad (\text{A.27})$$

and similarly $\nabla \mu = \mu_0 \nabla \chi$ Therefore in the absence of currents, and in paramagnetic, or diamagnetic liquids, the magnetic field induced force is

$$\mathbf{f} = \nabla P_0 + \nabla \left[\frac{\mu_0 H^2}{2} \rho \left(\frac{\partial \chi}{\partial \rho} \right)_T \right] - \frac{\mu_0 H^2}{2} \nabla \chi \quad (\text{A.28})$$

The inclusion of an electric current does not invalidate this derivation, as the current induces an inhomogeneity in the magnetic field, and can be treated as a perturbative modification of the field distribution, along with the introduction of the Lorentz force term.

Appendix B

Magnetic Field Calculations

Magnetic field calculations were carried out using the surface charge model (§2.1); where the magnet arrays were assumed to be composed of uniformly magnetised segments of hard, magnetically transparent, permanent magnetic material. Since the magnetisation is fixed and uniform within each segment the calculation reduces to finding the field due to a scalar magnetic charge density on each surface of every segment. The surface of each segment can be broken into simplexes, which in 3-D are right-angled triangles, and the field, H , at a point $P(x, y, z)$ is summed over the field due to each simplex. The strategy for field calculation is to, firstly, find an analytical expression for the field created by an individual simplex then, secondly, to break the magnet array into simplexes and simply sum over all the simplexes to find the field at any required point. The advantage of this model is that it gives an extremely smooth field.

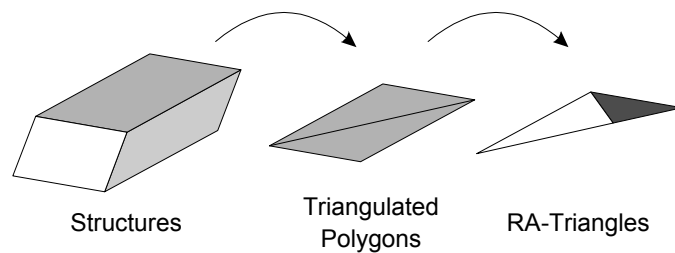


Figure B.1: A magnetic surface subdivided into right-angled triangle surface simplexes

B.0.3 Analytical Expressions for the Field

The analytical expression for the field due to a right-angled triangle can be written as follows, noting that all calculations are carried out for a triangle lying in the x - z plane, with the y -axis normal to the surface of the triangle (see fig. B.2).

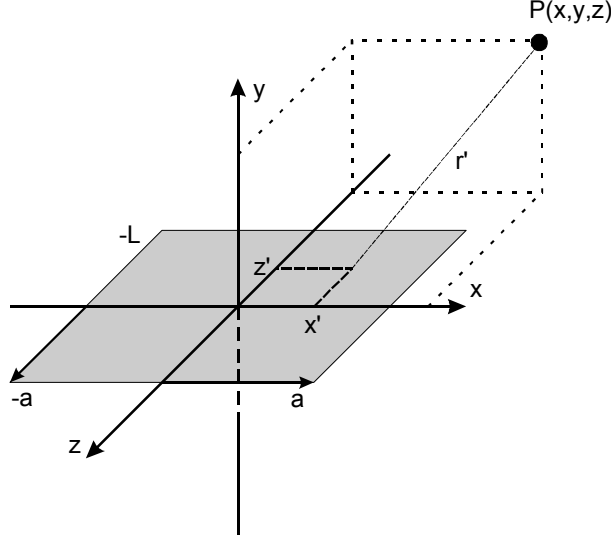


Figure B.2: A right-angled triangular magnetic charge sheet simplex in its local frame

The component parallel to the sheet, H_x , is given by:

$$H_x(P) = \frac{\sigma_m}{4\pi\mu_0} \left[\ln \left(\frac{b + \sqrt{(a-x)^2 + y^2 + (b-z)^2} - z}{\sqrt{(a-x)^2 + y^2 + z^2} - z^2} \right) + \frac{b}{\sqrt{a^2 + b^2}} \ln \left(\frac{r - \frac{ax+bz}{\sqrt{a^2+b^2}}}{\frac{a(a-x)+b(b-z)}{\sqrt{a^2+b^2}} + \sqrt{(a-x)^2 + y^2 + (b-z)^2}} \right) \right] \quad (\text{B.1})$$

There is a similar expression for H_z :

$$H_z(P) = \frac{\sigma_m}{4\pi\mu_0} \left[\ln \left(\frac{r - x}{a + \sqrt{(a-x)^2 + y^2 + z^2} - x} \right) + \frac{a}{\sqrt{a^2 + b^2}} \ln \left(\frac{\frac{a(a-x)+b(b-z)}{\sqrt{a^2+b^2}} + \sqrt{(a-x)^2 + y^2 + (b-z)^2}}{r - \frac{ax+bz}{\sqrt{a^2+b^2}}} \right) \right] \quad (\text{B.2})$$

where $r = \sqrt{x^2 + y^2 + z^2}$

and the magnetic surface charge density is given by:

$$\sigma_m = \mathbf{M} \cdot \hat{\mathbf{n}} \quad (\text{B.3})$$

where $\hat{\mathbf{n}}$ is the unit outward normal from the surface.

Finally the perpendicular component H_y is:

$$\begin{aligned}
 H_y(P) = \frac{\sigma_m}{4\pi\mu_0} & \left[\tan^{-1} \left(\frac{(x-a) + z + \sqrt{(x-a)^2 + y^2 + z^2}}{y} \right) - \tan^{-1} \left(\frac{x+z+r}{y} \right) \right. \\
 & + \frac{y}{\alpha\sqrt{B^2 - A^2 - C^2}} \left\{ \tan^{-1} \left(\frac{C + (A+B) \left(\sqrt{1 + \frac{(\alpha+\beta)^2}{\gamma^2}} + \frac{\alpha+\beta}{\gamma} \right)}{\sqrt{B^2 - A^2 - C^2}} \right) \right. \\
 & \left. \left. \times \tan^{-1} \left(\frac{C + (A+B) \left(\sqrt{1 + \frac{\beta^2}{\gamma^2}} + \frac{\beta}{\gamma} \right)}{\sqrt{B^2 - A^2 - C^2}} \right) \right\} \right] \quad (\text{B.4})
 \end{aligned}$$

where

$$\alpha = \sqrt{1 + \frac{b^2}{a^2}}, \quad \beta = -\frac{x + \frac{bz}{a}}{1 + \frac{b^2}{a^2}}, \quad \gamma = \sqrt{-\beta^2 + \frac{r^2}{1 + \frac{b^2}{a^2}}} \quad (\text{B.5})$$

and

$$A = -\gamma \frac{b}{a}, \quad B = \gamma \sqrt{1 + \frac{b^2}{a^2}}, \quad C = z + \beta \frac{b}{a} \quad (\text{B.6})$$

B.0.3.1 Transformations

The above equations above assume that the simplexes lie in the x - z plane, and so each polygon must be transformed from the global frame to a local frame (each polygon consists of two back-to-back right-angled triangle simplexes). This is carried out by four operations.

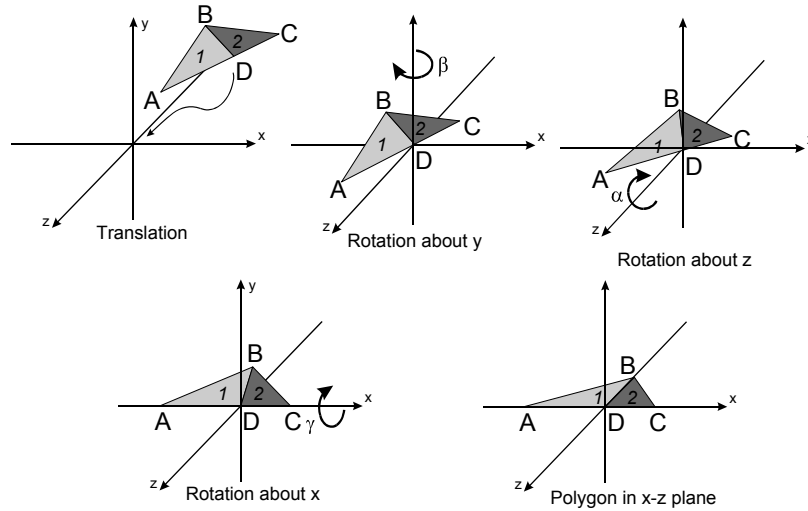


Figure B.3: The transformations needed to transform an arbitrary polygon from the global frame to the local frame.

We first translate our polygon to the origin, so that the point along the longest edge (edge AC) where the right angled triangles meet (point D) lies at the origin. We then rotate the polygon about the y -axis (by an angle β) so the edge AC lies in the x - y

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plane, then rotate the polygon about the z -axis (by an angle α) so that edge AC lies parallel to the x -axis. Then we rotate about the final axis, the x -axis (by an angle γ), such that point B is rotated into the x - z plane. The polygon then lies flat in the x - z plane.

The polygon consists of two back-to-back triangles; this means triangle 2 must be flipped as it is 'upside-down' with respect to our standard right-angled triangle simplex (see fig.B.3). If the polygon must undergo the rotations α , β , and γ triangle 1 must undergo the same rotations and the second 'upside-down' triangle 2 must undergo the rotations $-\alpha$, $\pi + \beta$ and $\pi - \gamma$ to flip it to the same orientation as the standard triangle. The component triangles must also be separately translated after the rotation; triangle 1 must be translated so that the vertex A lies at the origin and triangle 2 must be translated so that the vertex C lies at the origin.

The translation matrix is:

$$\begin{pmatrix} P_{x'} \\ P_{y'} \\ P_{z'} \\ 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & -S_x \\ 0 & 1 & 0 & -S_y \\ 0 & 0 & 1 & -S_z \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} P_x \\ P_y \\ P_z \\ 1 \end{pmatrix} \quad (\text{B.7})$$

The rotation matrix $\mathbf{R}_x(\gamma)$ for a rotation clockwise around the x -axis by γ is given by

$$\begin{pmatrix} P_{x''} \\ P_{y''} \\ P_{z''} \\ 1 \end{pmatrix} \gamma = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos(\gamma) & \sin(\gamma) & 0 \\ 0 & -\sin(\gamma) & \cos(\gamma) & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} P_{x'} \\ P_{y'} \\ P_{z'} \\ 1 \end{pmatrix} \quad (\text{B.8})$$

The rotation matrix $\mathbf{R}_y(\beta)$ for a rotation clockwise around the y -axis by β is given by

$$\begin{pmatrix} P_{x''} \\ P_{y''} \\ P_{z''} \\ 1 \end{pmatrix} \beta = \begin{pmatrix} \cos(\beta) & 0 & -\sin(\beta) & 0 \\ 0 & 1 & 0 & 0 \\ \sin(\beta) & 0 & \cos(\beta) & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} P_{x'} \\ P_{y'} \\ P_{z'} \\ 1 \end{pmatrix} \quad (\text{B.9})$$

The rotation matrix $\mathbf{R}_z(\alpha)$ for a rotation clockwise around the z -axis by α is given by

$$\begin{pmatrix} P_{x''} \\ P_{y''} \\ P_{z''} \\ 1 \end{pmatrix} \alpha = \begin{pmatrix} \cos(\alpha) & \sin(\alpha) & 0 & 0 \\ -\sin(\alpha) & \cos(\alpha) & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} P_{x'} \\ P_{y'} \\ P_{z'} \\ 1 \end{pmatrix} \quad (\text{B.10})$$

The rotation matrix $\mathbf{R}_1$ for triangle 1 is given by:

$$R_1(\alpha, \beta, \gamma) = R_x(\gamma)R_z(\alpha)R_y(\beta) \quad (\text{B.11})$$

And the rotation matrix $\mathbf{R}_2$ for triangle 2 is given by:

$$R_2(\alpha, \beta, \gamma) = R_x(\pi - \gamma)R_z(-\alpha)R_y(\pi + \beta) \quad (\text{B.12})$$

The inverse rotation matrix $\mathbf{R}^{-1}$ is given by:

$$R_1^{-1}(\alpha, \beta, \gamma) = R_y(-\beta)R_z(-\alpha)R_x(-\gamma) \quad (\text{B.13})$$

Appendix C

Shoup-Szabo Fitting Routine

```
1  /*-----
2
3   * Linear Fit Test
4   * 25-11-09 Peter Dunne
5   *-----*/
6  #include <stdlib.h>
7  #include <math.h>
8  #include <stdio.h>
9
10 /******
11 * Globals
12 *****/
13 #define PI 3.141592654
14 #define N 100 /* No. of iterations */
15 #define n1 40000 /* No. of data points */
16 #define L 1e-6 /* Convergence limit for the perturbation fit ↵
17   */
18 #define F 96485.3415
19 // #define c0 5.47e-6 /* Moles/cm^3 ↵
20   */
21 // #define a 1.963e-3 /* Area cm^2 ↵
22   */
23 #define a 0.281 /* Radius mm */
24 // #define n0 1
25 #define init 0 /* No. of data ↵
26   points to skip for fitting routine */
27 #define off 2 /* Time offse to first ↵
28   pulse (s) */
29 #define skip 407 /* No. of data ↵
30   points to skip*/
```

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```
25 #define np 390                                /* No. of data points↵
    in pulse */
26 /*****
27 * Function Prototypes
28 *****/
29 int lfit(double x[], double y[], double fitres[], int n);
30 void cott(double x[], double xs[], double y[], double ys[], int n↵
    );
31 void pert(double xs[], double y[], double yp[], double A, double ↵
    B, int n);
32 int fit(double xs[], double yp[], double A, double B, int n );
33 int readfile(double x[], double y[]);
34 void writefile(double x[], double y[], double yp[], int n);
35 double D(double A, double B);
36 double C(double A, double B, double n0);
37 double Neff(double A, double B, double c0);
38
39 char outp[30];
40 /*****
41 * Main Routine
42 *****/
43
44 int main(int argc, char **argv) {
45     int i=0,n=0;
46     double *x,*y,*xs,*ys,*xp,*yp, A, B, *fitres, c0, n0;
47     x = (double *) malloc (n1*sizeof(double));
48     y = (double *) malloc (n1*sizeof(double));
49     xs = (double *) malloc ((n1)*sizeof(double));
50     ys = (double *) malloc ((n1)*sizeof(double));
51     xp = (double *) malloc ((n1)*sizeof(double));
52     yp = (double *) malloc ((n1)*sizeof(double));
53
54     fitres = (double *) malloc (2*sizeof(double));
55
56
57 // ****
58 printf("\n=====\\n");
59 printf("|\\tShoup-Szabo Chronoamperometry\\t |\\n");
60 printf("|\\tData Fitting\\t\\t\\t |\\n");
61 printf("=====\\n");
62 n=readfile(x,y);
63 cott(x,xs,y,ys,n);
64 A = B = 0;
```

```

65     printf("\nPerforming Linear Fit...\n");
66     lfit(xs,ys,fitres,n);
67     A = fitres[1];
68     B = fitres[0];
69     printf("A=%le\tB=%le\n",A,B);
70     printf("\nLooping modified Linear Fit...\n");
71     pert(xs,ys,yp,A,B,n);
72     lfit(xs,yp,fitres,n);
73
74     i=0;
75     while ( fabs((B-fitres[0])/fitres[0]) > L && fabs((A-fitres[0]←
        [1])/fitres[1]) > L && i < N ) {
76         printf("\nLoop No. %d\n", i+1);
77         A = fitres[1];
78         B = fitres[0];
79         printf("A=%le\tB=%le\n",A,B);
80         pert(xs,ys,yp,A,B,n);
81         lfit(xs,yp,fitres,n);
82         i++;
83     }
84
85     A = fitres[1];
86     B = fitres[0];
87     printf("Iterations = %d\n",i);
88     printf("A=%le\tB=%le\n",A,B);
89
90     fit(xs, yp, A, B, n);
91     printf("Concentration mol/l:\n");
92     //scanf("%lf",&c0);
93     c0 = 0.1;
94     printf("No. of electrons Transferred:\n");
95     //scanf("%lf", &n0);
96     n0 = 1;
97     printf("Inputs:\n");
98     printf("A=%le\tB=%le\n",A,B);
99     printf("Area = %le\tC= %le \tN = %le\n", a, c0, n0);
100    printf("D=%le\tC=%lg\tN1=%lf\n", D(A,B), C(A,B,n0), Neff(A,B,c0←
        ));
101
102    writefile(x,y,yp,n);
103
104    //Free memory allocated for data arrays
105    free(x);

```

C. SHOUP-SZABO FITTING ROUTINE

```
106  free(y);
107  free(xs);
108  free(ys);
109  free(xp);
110  free(yp);
111  free(fitres);
112  exit(0);
113 }
114
115 /*****
116  * Linear Least Squares Fit Routine
117  * need to pass data pair x[i], y[i]
118  * Calculates A,B
119  *****/
120 int lfit(double x[], double y[], double fitres[], int n) {
121     int i=0;
122     int s=0;
123     double SUMx, SUMy, SUMxy, SUMxx, SUMyy, SUMres, res, y_estimate←
        ;
124     SUMx = 0; SUMy = 0; SUMxy = 0; SUMxx = 0; SUMyy = 0;
125     for (i=0; i<=n; i++)
126     {
127         SUMx = SUMx + x[i+s];
128         SUMy = SUMy + y[i+s];
129         SUMxy = SUMxy + x[i+s]*y[i+s];
130         SUMxx = SUMxx + x[i+s]*x[i+s];
131         SUMyy = SUMyy + y[i+s]*y[i+s];
132     }
133
134     printf("SUMx = %lf \n SUMy = %lf \n SUMxy = %lf \n SUMxx = %lf ←
        \n SUMyy = %lf \n",SUMx,SUMy,SUMxy,SUMxx,SUMyy);
135     fitres[0] = ( SUMx*SUMy - (n-s)*SUMxy ) / ( SUMx*SUMx - (n-s)*←
        SUMxx ); /* B */
136     fitres[1] = ( SUMy - fitres[0]*SUMx ) / (n-s); ←
        /* A */
137     fitres[2] = ( (n-s)*SUMxy - SUMx*SUMy ) / ( sqrt ( ( SUMxx - ←
        SUMx*SUMx )*( (n-s)*SUMyy - SUMy*SUMy ) ) ); /* R^2 */
138     Dex = D(A,B);
139     Cob = C(A,B);
140     Rex = R(A,B,Dr);
141     neff = N(A,B,ea,e01);
142     printf("D1 = %1.4le\tC2 = %1.4le\tRex = %1.4le\nNeff = %1.4lg←
        n",Dex, Cob, Rex,neff);
```

```

143     printf ("-----\n");
144
145
146     SUMres = 0;
147     for (i=0; i<n; i++)
148     {
149         y_estimate = fitres[0]*x[i+s] + fitres[1];
150         res = y[i+s] - y_estimate;
151         SUMres = SUMres + res*res;
152
153     }
154
155     printf("=====\n");
156     printf("Residual sum = %1.4le\n", SUMres);
157
158     return(0);
159
160 }
161
162
163 /*-----
164  *   Convert t to t-1/2
165  *-----*/
166 void cott(double x[], double xs[], double y[], double ys[], int n↔
167     ) {
168     int i;
169     FILE *out;
170     char outp[]="cott.txt";
171     out = fopen(outp,"w");
172     fprintf(out,"x\ty\tfit\n");
173     xs[0]=0;
174     ys[0]=fabs(y[0]);
175     for (i=0; i<n; i++) {
176         xs[i]=1/sqrt(x[i]);
177         ys[i]=fabs(y[i]);
178         fprintf(out,"%le\t%le\t%le\t%le\n",x[i],y[i],xs[i],ys[i]);
179     }
180     fclose(out);
181 }
182
183 /*-----
184  *   Perturbation of I(t) to I(t) - 0.2732*A*exp(-0.3911*PI1/2 *B↔
185         /t-1/2 * A)

```

C. SHOUP-SZABO FITTING ROUTINE

```
184  /*-----*/
185  void pert(double xs[], double ys[], double yp[], double A, double B, int n) {
186      int i;
187      for ( i=0; i<n1; i++) {
188          yp[i] = ys[i] - 0.2732*A*exp(-0.3911*sqrt(PI)*xs[i]*B/A);
189      }
190  }
191
192
193  /*-----
194  *   Export Fit
195  *-----*/
196  int fit(double xs[], double yp[], double A, double B, int n ) {
197      int i;
198      for ( i =0; i<=n; i++) {
199          yp[i] = A + B*xs[i];
200      }
201      return(0);
202  }
203
204  /*-----
205  *   Initialise read file
206  *-----*/
207  int readfile(double x[], double y[]) {
208      int i,j;
209      double dummy[n1];
210      char inp[30], tmp[256]; //filename
211      FILE *infile;
212
213      printf("Enter filename of data to fit:\n");
214      scanf("%s",inp);
215      infile = fopen(inp,"r");
216      if(fopen(inp,"r")==0) {
217          printf("Cannot read %s.\n",inp);
218          return(1);
219      }
220      strcpy(inp, outp);
221      i=0;
222      j=0;
223      while ( j<skip) {
224          j++;
225          fgets(tmp, 256, infile);
```

```

226     }
227
228     i=0;
229
230     while ( fscanf (infile, "%lg %lg", &x[i], &y[i]) != EOF && i <=
                < np) {
231         x[i] = x[i] - off;
232         i++;
233     }
234     return i;
235 }
236
237 /*-----
238  *   Initialise output file
239  *-----*/
240 void writefile(double x[], double y[], double yp[], int n) {
241     int i;
242     FILE *out;
243     char suff[5] = ".out";
244     char outp[]="results.txt";
245     out = fopen(outp,"w");
246     fprintf(out,"x\ty\tfit\n");
247
248     if (y[1]/fabs(y[1]) > 0 ) {                                /* Is the current↵
                positive? */
249         for (i=0; i<n; i++) {                                    /* Yes */
250             fprintf(out,"%le\t%le\t%le\t%le\n",x[i],y[i],yp[i],y[i]-yp[i]↵
                );
251         }
252
253     }
254
255     else {                                                        /* No */
256         for (i=1; i<n; i++) {
257             fprintf(out,"%le\t%le\t%le\t%le\n",x[i],y[i],-yp[i],y[i]+yp[i]↵
                );
258         }
259     }
260     fclose(out);
261 }
262
263 double D(double A, double B)
264 {

```

C. SHOUP-SZABO FITTING ROUTINE

```
265  double val;
266  val = (A*a/B)*(A*a/B)/(PI*100);
267  return val;
268  }
269
270  double C(double A, double B, double n0)
271  {
272  double val;
273  val = fabs(B*B/(F*n0*a*a*a*A))*1e6;
274  return val;
275  }
276
277
278  double Neff(double A, double B, double c0) {
279  double val;
280  val = fabs(B*B/(F*c0*a*a*a*A))*1e6;
281  return val;
282  }
```