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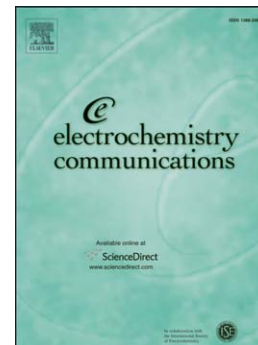
Magnetic fields in electrochemistry: The Lorentz force. A mini-review

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Magnetic fields in electrochemistry: the Lorentz force. A mini-review

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Abstract. Some recent work on the flow induced by uniform or non-uniform magnetic fields acting on currents in an electrochemical cell is reviewed. The effects include modifying the structure and texture of electrodeposits including their chirality, controlling hydrogen bubble release, inducing microfluidic flow and influencing nucleation. Much of this depends on micro-magnetohydrodynamic flow, on a scale of microns.

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Keywords: Electrodeposition, nucleation, polymerization, chirality, hydrogen evolution, gas oscillator

1 Introduction

Although the influence of an applied magnetic field on the operation of an electrochemical cell has been studied for over 40 years,^[1,2] magnetochemistry remains relatively unfamiliar territory to all but a few specialized research groups. The topic is inherently interdisciplinary, melding concepts from electrochemistry, hydrodynamics and magnetism. The results are sometimes surprising, and their elucidation can lead to unexpected insights into fundamental electrochemical processes, as well as new practical applications. It is useful to distinguish the effects of a uniform magnetic field from those of a magnetic field gradient, and to consider the forces of magnetic origin in relation to others acting in the cell.^[3] In this short review we focus on the electromagnetic forces acting on electric currents. The magnetophoretic forces acting on paramagnetic ions are the topic of a companion review.^[4] Both types of force are usually present, because any redox process where a single electron is transferred necessarily involves paramagnetic species, but one or the other is often dominant.

2 Uniform magnetic fields

2.1 Cathodic processes

The usual way for magnetic fields to create convection in an electrochemical cell is by the magnetohydrodynamic (MHD) effect (Fig. 1). The field \mathbf{B} in an electrochemical cell is the externally imposed field, essentially unaltered by the flow of electrolyte or current. The interaction of the field with the local current density \mathbf{j} induces a flow that tends to reduce the diffusion layer thickness and enhance mass transport. The limiting current in the diffusion-controlled regime increases due to localized magnetic stirring of the electrolyte. This convective force density has the same origin as the driving force in an electric motor. It is known as the Lorentz Force and is given by the following equation:

$$\mathbf{F}_L = \mathbf{B} \times \mathbf{j} \quad (1)$$

The force is zero when \mathbf{B} and \mathbf{j} are parallel, and it is largest when they are orthogonal. During electrodeposition, the Lorentz force may be comparable in magnitude to the buoyancy force driving convection, due to density variations of order 10 % in the electrolyte near the cathode. A typical value of \mathbf{F}_L for $B = 1$ T and $j = 1$ mA mm⁻² is 1000 N m⁻³. The flow pattern can therefore be modified by applying a magnetic field, or by realigning the field to alter the relative orientation of the Lorentz force and gravity.^[5,6] A consequence of \mathbf{F}_L is an increase in electrodeposition rate, varying as $B^{1/3}$.^[7]

The benefits of large-scale convection can be effectively achieved by mechanical agitation, but the relation between Lorentz force and local current density means that it is possible to induce flow magnetically patterns on a scale that would be otherwise unattainable. These effects may be sharply localized in spots of high current density, where a micro-MHD effect is created (Fig. 1c). Another advantage is that electrolyte flow can be driven in microfluidic channels, where transverse redox currents are flowing.^[8,9]

Since \mathbf{j} is inevitably non-uniform at the edge of an electrode, there is normally MHD flow around the rim when \mathbf{B} is perpendicular to the electrode surface (Fig. 1b). Furthermore, uneven growth at the cathode during electrodeposition produces a locally nonuniform current distribution, giving rise to secondary micro-MHD vortices around growing asperities that protrude into the diffusion layer, as illustrated in Fig. 1c.^[10,11] Mogi et al have recently demonstrated that magnetically-prepared Ag or Cu electrodes exhibit a high sensitivity towards certain enantiomeric aminoacids, offering a novel route for the synthesis of biomolecules with a high enantioselectivity.^[11,12] The effect may be explained by chirality imprinted on the electrode surface, where screw dislocations grow in a sense imposed by the direction of the magnetic field.^[11] Furthermore, it is suggested by Aogaki et al

that the no-slip boundary condition at the electrode surface is relaxed during electrodeposition by the formation of ionic vacancies, which facilitate the establishment of these microvortices.^[13] The vacancies are thought to coagulate into nanobubbles of radius r which are stabilized by a layer of charged anions on their inner surface. The Coulomb repulsion reduces the effective surface tension γ and therefore cuts down the Laplace pressure $2\gamma/r$, which would otherwise lead to the rapid dissolution of the nanobubble. The enantiomeric sensitivity increases with decreasing electrode diameter, due to the supporting effect of the primary MHD flow, Fig 1b. A rotating cell can also impose the electrode chirality.^[12]

Hydrogen bubble formation and release during the electrolysis of water is strongly influenced by magnetically-induced flow.^[14] Gas bubbles occlude the electrode surface, deforming the local current density. At electrodes where the average current distribution is uniform, it is found that the bubbles released are smaller when a magnetic field is present.^[15-17] This is beneficial during electrodeposition, as the films produced lack the typical defects caused by hydrogen evolution.^[18] Even when the field is normal to the cathode and MHD is negligible, there are still micro-MHD flows arising from the deformation of the current distribution by the spherical bubbles, which induce hydrodynamic drag forces that sweep the bubbles away from the electrode surface, thereby impeding their growth.

With a microelectrode comparable in diameter to the bubbles (< 1 mm), the bubble release is often periodic and the system behaves as a gas oscillator,^[19] depending on the relative orientation of F_L and buoyancy (Fig 2).^[20] In that case it is possible to see the opposite effect — hydrogen bubbles grow bigger in a vertical field applied normal to the microelectrode surface.^[21] Motion tracking images using PVC particles reveal that the flow created when the current distribution is deformed around the growing bubble tends to pin it to the microelectrode. Electrochemical noise analysis provides a frequency spectrum,^[22] and it suggests that bubbles grow by coalescence with much smaller ones,^[20,21,23] something that can be observed directly, together with microbubble growth and release, using high-speed photography.^[21,24] Magnetic field does modify the bubbling regime, but surface tension appears to be the critical factor.

The efficiency of water electrolysis to produce hydrogen can also be improved magnetically via MHD.^[25] Micro-MHD is also responsible for the improvement of hard nickel electrodeposits containing alumina nanoparticles when they are pulse-plated in a magnetic field. The alumina content of the hard coating is increased, and its hardness is improved, partly due to the effective removal of hydrogen bubbles during plating.^[26]

Besides enhancing the deposition rate via the MHD effect, there are many studies which show the influence of magnetic fields on the morphology, texture, roughness and dendritic electrodeposits.^[27] The results depend on the orientation of the field relative to the cathode surface. Aogaki et al suggest that fields applied parallel to the electrode tend to suppress three-dimensional nucleation and dendritic growth, but they promote faster, two-dimensional growth and smoother deposits due to a micro-MHD effect.^[10] A perpendicular field usually produces rougher deposits. The field often induces preferred crystallographic texturing in metallic electrodeposits,^[28] and the effects are enhanced in continuous films as the deposit grows thicker.^[29] The texturing is usually accompanied by changes in grain shape, typically from rounded to needle-like in a perpendicular field.^[18,30] An example is provided by the deposition of Co, where there is a clear tendency of the film to grow along the 110 *hcp* direction when the magnetic field is parallel to the electrode surface.^[18] In this configuration, the surface roughness of electrodeposited films may be enhanced^[18] or reduced,^[29] but the film thickness is almost always enhanced as a result of improved ion transport.^[29,31] When ferromagnetic films grow in a magnetic field, it will be will be deformed by surface asperities on the film, and field gradient effects then come into play.^[4] Surface roughness is correlated with changes in extrinsic magnetic properties such as coercivity,^[29] with smoother films presenting less hysteresis.

Some examples where the magnetic field has been found to modify the morphology of individual crystals via micro-MHD convection are Cu_2O ^[32] and Zn.^[33] Images are shown in Fig 3. The field can also affect the morphology of electrodeposited materials such as hydroxyapatite.^[34,35] The preferred crystal habit of electrodeposited hydroxyapatite is plate-like, but this changes to needle-like when the field is parallel to the electrode surface, and spherical when the field is in the perpendicular direction.

A magnetic field is found to influence not only growth, but also *nucleation* of both metals and gas from solution. During metal electrodeposition, it is frequently found that the number of nucleation sites increases in the presence of the field, irrespective of its orientation.^[33,36] Electrodeposition performed on TEM grids by Ustarroz et al has shown that the nucleation sites originate from the assembly of tiny mobile subnuclei.^[37] Therefore, the fact that experiments performed in magnetic fields produce a larger number of particles would imply that the early nuclei are somehow stabilized by the field, with growth setting in before they are able to assemble. The physical basis of this magnetic influence on nucleation is not clear, although the subsequent growth may be influenced by micro-MHD, as suggested by Aogaki.^[10] However, on the nanometer scale of

the Helmholtz double layer, it is appropriate to substitute concepts of molecular dynamics for those of fluid mechanics (viscosity, surface tension, etc).

2.2 Anodic processes

Turning to effects of magnetic fields on anodic processes, it is worth mentioning the shifts of rest potential^[38] and enhanced corrosion^[39,40] of magnetic and nonmagnetic electrodes. Here again, micro-MHD is influencing mass transport. When corrosion takes place via chemical etching, the field improves the transport of oxidant towards the surface, evidenced by anodic shifts in the rest potential of order 100 mV. Although anodic shifts due to microconvection driven by the Lorentz force are found for *any* corroding electrode, there is an additional effect when a small ferromagnetic electrode such as iron is used, which creates a strong stray field in its vicinity. Dissolved iron ions are retained in these regions,^[4] and H⁺ ions are displaced from them, leading to a local increase in pH, a decreased corrosion current and a cathodic shift of the rest potential.^[41,42] Images^[38] and surface profiles^[41] of the corroded electrodes show the effect of magnetic field on the cathodic and anodic areas. During electrochemical etching, the field also shifts the formation of the passive layer towards much higher anodic potentials as it prevents the build-up of corrosion products near the surface.^[39,43]

Polymerization is another anodic process that has been influenced by magnetic fields. The polymerization rate is enhanced via MHD convection^[44] while modifications in polymer texture, open or crystalline, are achieved varying the direction of the field.^[45] Massive changes in roughness arise when liquid crystals are present in the electrolyte during the synthesis,^[46] and this effect also depends on the field orientation. The action of the field on the anisotropic diamagnetic susceptibility of the polymers or liquid crystals in solution can lead to their orientation.

Magnetic fields can affect charge transfer reactions taking place on confined redox probes.^[47] The oxidation of ferrocene alkane self-assembled monolayers (SAMs) when the field is parallel to the electrode surface shows an irreversible decrease of more than 50 % of the active sites. The change is interpreted in terms of conformational modification within the monolayer, rather than of the electron transfer step. During oxidation at the electroactive SAMs, ion pair interactions are established between the positive charges in the SAM and anions in solution. The relative orientation of the hydrocarbon chains with respect to the surface switches from a tilted to a more upright configuration. MHD helps to prevent this conformational change.

Practical applications of MHD include control of corrosion and electropolishing improving the surface finish of electropolished biocompatible metallic alloys^[48] and the performance of nickel metal hydride batteries is reportedly enhanced by more than 25% when compared with the performance without magnetic fields.^[49]

3 Nonuniform magnetic fields

Convection generated by the Lorentz force in nonuniform fields can be used to create flow patterns in the electrolyte that would otherwise be unattainable. An example is the field gradient produced by two oppositely-polarized magnets that create fields in opposite directions parallel to the cathode and anode. The result is creation of a vortex about a axis horizontal axis parallel to the electrodes. The sign of the magnetically-induced vortex can be arranged to counteract that created by buoyancy, resulting in a uniform electrodeposit.^[50,51] Fine-grained structures with improved homogeneity can be obtained by pulsing the current.^[52]

4 Conclusions

Much recent work on the influence of magnetic fields acting on currents has been focussed on micro-MHD, where qualitative descriptions of the phenomena have been advanced. Millimeter-scale control of flow may be achieved using an externally applied field with ferromagnetic flux concentrators in the bath. For large-scale processes, the use of permanent magnets is essential. Our current understanding of the effects of magnetic fields on nucleation of both metals and gas from solution is sketchy. Bulk hydrodynamic modelling will have to be supplemented by molecular dynamics to understand the dynamic boundary condition at the electrode surface, in order to develop a better, quantitative understanding of magnetic field effects on the structure and morphology of the electrodeposits. There are opportunities to use nanoimprinted electrodes for nucleation studies and lithographically-patterned electrodes for magnetically-controlled release of monodisperse bubbles.

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Figure Captions

Figure 1. Hydrodynamic flow at an electrode in a uniform magnetic field. a) Field applied parallel to the electrode surface. The primary MHD flow is parallel to the surface. b,c) Field applied perpendicular to the electrode surface. In b) the primary MHD flow is a vortex around the rim but in c) secondary micro-MHD vortices arise around protuberances on the surface.

Figure 2. Illustration of the effect of magnetic field on hydrogen release from a vertical microelectrode surface. a) Bubble release is periodic when the field is oriented so that the Lorentz-force-induced flow acts in the opposite direction to buoyancy or if there is no field, and it is random when it adds to it. Panel b) shows the electrochemical noise spectra in the two cases. Adapted with permission from *Electrochimica Acta* 55 (2010) 8664, Copyright (2010) Elsevier.

Figure 3. Examples of magnetic field effects on the morphology of electrodeposits showing images of Zn (top) and Cu₂O (bottom) crystals grown in different magnetic fields. Adapted with permission from *J Phys Chem C* 116 (2012) 18308–18317, Copyright (2012) American Chemical Society and *Cryst Eng Comm* 13 (2011) 3373–3377, Copyright (2011) The Royal Society of Chemistry.

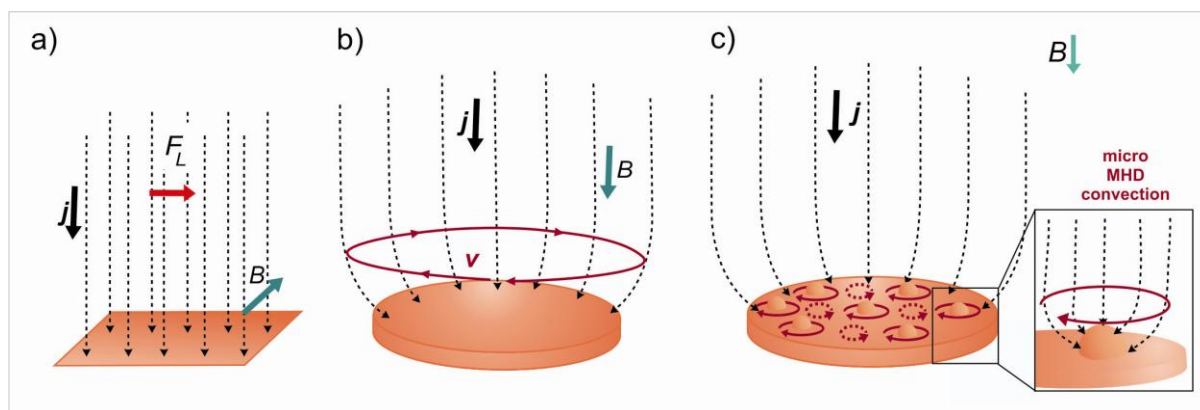


Figure 1

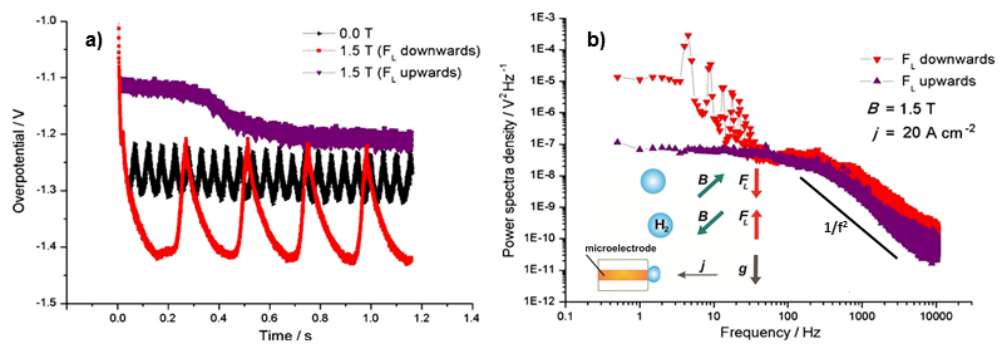


Figure 2

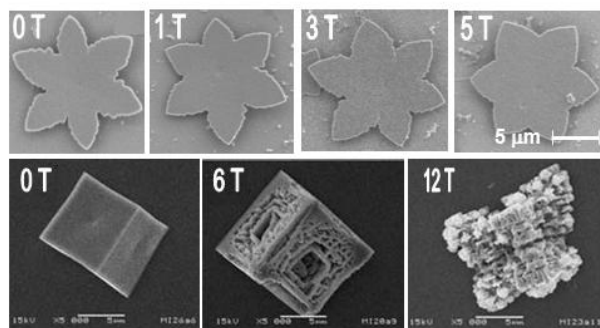


Figure 3

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Highlights

- An up-to-date mini review of recent results in magnetochemistry, based on the Lorentz force
- Focus on micro-magnetohydrodynamics (micro-MHD)
- Discussion of magnetic field effects on chirality, hydrogen bubble release and nucleation
- Suggestion of future work on molecular dynamics

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