The Oxygen Evolution Reaction at Manganese oxide Films in Base: Kinetics & Mechanism

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Abstract

Various manganese oxide type Dimensionally Stable Anode (DSA) electrodes were prepared through a simple thermal decomposition technique at different annealing temperatures for their effect on the oxygen evolution reaction (OER). Along with the change in different annealing temperatures, the effects of different metal substrates were also explored. Cyclic Voltammetry was used to analyze the redox transitions of all annealing temperatures on the nickel and titanium substrates. Steady state polarization curves (also known as Tafel Plots) were used to determine tafel slopes, Open Circuit Potential decay analysis was also used to determine tafel slopes. Reaction orders of the 350°C nickel Mn_xO_y electrode were determined and calculated as a half reaction order. A mechanism for this electrode is also proposed. SEM-EDX and FTIR analysis are also reported on some Mn_xO_y films and powders.

Introduction

Currently the interest in developing an alternative to fossil fuels has increased dramatically in recent years due to the imminent threat of the depletion of the earth's coal, oil and gas reserves. As a consequence, the costs of these fossil fuels have also increased. Another disadvantage associated with fossil fuels is the issue of carbon based emissions from the fossil fuels when burnt into the earth's atmosphere which leads to global warming. Many renewable alternatives have already been developed as fossil fuel alternatives e.g. wind power, solar power and hydropower. However all these alternatives may not suit people in different parts of the planet due varied geological/weather conditions being unreliable. Alkaline water electrolysis has been proposed as one of the solutions to this problem; the equations for this process are shown below;

The cathodic process produces large amounts of hydrogen gas which can then be used in vital applications such as energy conversion and energy storage devices. In contrast to the use of fossil fuels, the production of hydrogen, as an energy source, from alkaline water electrolysis offers an environmentally inoffensive and reliable route to the production of the large volumes of hydrogen gas required by a possible hydrogen economy (1-3).

Of course during water electrolysis oxygen is also produced at the anode, according to equation 1 above, the production of oxygen is the main energy consuming step in the reaction. In practice, the efficiency of water electrolysis is limited by the large anodic over-potential of the oxygen evolution reaction (OER) (3). Thus, a vast amount of research is being dedicated into fully understanding the kinetics and mechanism of the OER reaction. This knowledge should lead to the development of an OER anode material that produces oxygen at the lowest overpotential.

Currently there are various electrodes being studied for the oxygen evolution reaction, these include thermally prepared DSA type oxide electrodes, electrochemically prepared hydrous oxide electrodes, and electrodeposited bulk oxide/hydroxide electrodes using various metal oxides (4). In this work DSA type electrodes are examined. DSA electrodes were first used by the chlori-alkali industry. These electrodes consist of a titanium support which was then coated with a mixed metal oxide (5). The optimum oxide materials for the preparation of these electrodes are RuO_2 and IrO_2 due to their ability to produce oxygen at the lowest overpotential compared to other metal oxides. However these materials are highly expensive and do not exhibit long term stability in alkaline water electrolysis conditions (5). Much interest into the use of the first row transition metals (Mn, Fe, Ni and Co) have been reported for OER anode material due to their good electrochemical performance and their long term stability in alkaline media (4).

In recent years manganese oxide has been studied as an alternative anodic material for alkaline water electrolysis due to its relative low cost, eco-friendly properties and long term corrosion resistance in alkaline solution compared to RuO_2 and IrO_2 (6).

Manganese oxides electrodes can be produced/synthesized in various ways such as Electrodeposition (7), Chemical precipitation (8), Sol-gel (9) and by Thermal Decomposition (10). In this communication, the behaviour of thermally decomposition prepared DSA type manganese oxide electrode as an OER anode material will be reported.

Experimental Details

Preparation of electrodes

The working electrodes in this work were prepared via a thermal decomposition method outlined by Trasatti *et al.* (9) To prepare the electrodes titanium (as supplied by Alfa Aesar- Johnson Matthey company, purity 99.99% (metals basis), with a diameter of 1.0mm) or nickel wire (as supplied by Alfa Aesar- Johnson Matthey company, purity 99.99% (metals basis)) were sealed in glass. The electrodes were then dipped in 5M H_2SO_4 , polished with 1200 grit carbimet paper and washed with deionised water and set aside to dry. A 0.01M Mn_xO_y precursor solution was made from dissolving $\text{Mn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in a 10ml conical flask, which was weighed using a weighing balance (Sartorius, model 1872). The resulting mixture was evaporated on a hot plate (Jenway

hotplate and stirrer, model 1000) until a black/brown slurry was observed. Deionised water was then added to the slurry to form a paste (will be referred to as Mn_xO_y paste), which was then used to paint onto either the titanium or nickel wires that were used as the working electrodes, which were previously prepared.

The annealing treatment applied in this research consisted of painting the working electrode with one coat of the Mn_xO_y paste and dried in an oven at 90°C for ten minutes in air. Another coat of the Mn_xO_y paste was coated onto the electrode and annealed in air, in a second oven, for 4 hours. A number of samples were prepared at various annealing temperatures on both titanium and nickel substrates. This is illustrated in figure 1 below;

Figure 1: Experimental schematic of the preparation of the Mn_xO_y Films

Electrochemical testing analysis methodology

All electrochemical experiments were undertaken in a standard three electrode cell. The working electrodes consisted of the titanium or nickel film substrate with Mn_xO_y paste annealed at different temperatures, as described above. A graphite rod was employed as a counter electrode and a mercury-mercuric oxide (Hg/HgO) reference electrode (CH instruments, cat no. 152) was utilized as a reference standard¹, therefore all potentials are quoted against this reference electrode. The various electrolyte solutions used for the redox behavior studies of the Mn_xO_y films including tafel slope analysis and reaction order studies with respect to the hydroxide ion ($-\text{OH}^-$), were prepared from sodium hydroxide (NaOH) pellets (Sigma-Aldrich, $\geq 98\%$ purity, reagent grade). The NaOH electrolyte solutions concentrations ranged from 0.01M to 5M.

The electrochemical measurements were performed using high performance digital potentiostats including a CH model 1760 D Bi-potentiostat system monitored by the CH1760D electrochemical workstation beta software or an Autolab PGSTAT302N potentiostat/ galvanostat monitored by the Nova 1.8 Autolab software. Cyclic Voltammetric experiments were ran in aqueous 1.0 M NaOH at 100 mV s^{-1} between limits of -2.0 V and +2.0 V vs. Hg/HgO reference electrode. Tafel plot measurements

¹ The equilibrium potential of the cell $\text{Pt}/\text{H}_2/\text{OH}^-/\text{HgO}/\text{Hg}$ is 0.926 V at 298 K. Since the equilibrium oxygen electrode potential is 1.229 V vs RHE, it follows that the corresponding value is 0.303 V vs. Hg/HgO in the same solution. Hence $E_{\text{Hg}/\text{HgO}} = E_{\text{RHE}} - 0.926 \text{ V}$. It is a common practice in the literature on the OER to express potential in terms of the oxygen overpotential n , when the reference electrode is a Hg/HgO electrode in the same solution as the working anode. Clearly, in this case the overpotential n is related to E_{meas} measured on the Hg/HgO scale as follows: $n = E_{\text{meas}} - 0.303 \text{ V}$ (at $T = 298 \text{ K}$)

were performed at a sweep rate of 1mV s^{-1} in the forward oxidation direction. For tafel plot measurements the uncompensated solution resistance was usually determined at a 90% compensation level. All tafel plot data is presented in iR compensated form.

Electrochemical Impedance measurements

The electrochemical impedance measurements were performed using high performance digital potentiostats including a CH model 1760 D Bi-potentiostat system monitored by the CH1760D electrochemical workstation beta software. The electrochemical impedance measurements were ran in 1 M NaOH at a fixed potential of -0.1 V.

SEM-EDX measurements

The morphological characteristics of the DSA Mn_xO_y type electrodes were carried out by a SEM Karl Zeiss Ultra at an accelerating voltage between 15KV – 2KV and a working distance between 9mm -5mm.

FTIR analysis

Fourier Transform Infrared Spectroscopy analysis was also carried out on the DSA Mn_xO_y electrode with a Spectrum 100 FTIR spectrometer using Spectrum software to record the data. The spectrum was recorded in the range between 4000cm^{-1} and 500cm^{-1} .

Results

In the present work, we focus on the redox properties and electrocatalytic behaviour with respect to anodic oxygen evolution of manganese dioxide electrodes in aqueous alkaline solution. The redox behaviour of the resulting oxide films is investigated as a function of substrate and annealing temperature using Cyclic Voltammetry. Interestingly, the voltammetric profile for the manganese dioxide film is strongly dependent on the nature of substrate, as evident from Figure 2.

Redox characteristics – Nickel and titanium substrate

The change in annealing temperatures exhibits a different voltammetric profile for the same metal substrate which could be due to different Manganese compounds being formed due to the different temperatures applied to the manganese oxide solution painted on the substrate, as shown from Fig. 2.

According to Hong *et al.* if pure manganese nitrate is exposed to 250°C , 600°C degrees and 1000°C the manganese compounds which are produced are MnO_2 , Mn_2O_3 and Mn_3O_4 respectively(11), these chemical equations are shown below;

Heating the manganese dioxide at approximately 600°C and 1000°C temperatures allows for the loss of oxygen to produce Mn_2O_3 and Mn_3O_4 ;

Table 1 shows the different oxidation states of the various manganese compounds formed at the different temperatures. Oxidation numbers have been assigned to the corresponding Mn_xO_y compound from Pourbaix diagrams hence possible redox transition states can be assigned to the different annealing temperatures (12);

TABLE I. Oxidation numbers of corresponding manganese compounds at different annealing temperatures from literature.

Mn_xO_y Compound	Oxidation number (12)	Annealing temperature(°C) (11)
MnO_2	+4	250
Mn_2O_3	+3	600
Mn_3O_4	+2.67	1000

Figure 2: Typical CV response recorded in 1.0 M NaOH at a sweep rate of 100 mVs^{-1} for ((a) Ni-350°C) nickel film substrate at 350°C annealing temperature ((b) Ni-450°C) nickel film substrate at 450°C annealing temperature and ((c) Ni-600°C) nickel film substrate at 600°C annealing temperature ((d) Ti-350°C) titanium film substrate at 350°C annealing temperature ((e) Ti-450°C) titanium film substrate at 450°C annealing temperature and ((e) Ti-600°C) titanium film substrate at 600°C annealing temperature.

As outlined, the manganese oxide film prepared on the nickel substrate at 350°C exhibits two oxidation peaks at -0.7 V(A₁) which is small compared to the sharp second oxidation peak at 0.45 V(A₂) and one sharp reduction peak at 0.35 V(C₁). Similarly the manganese oxide film prepared on the Nickel substrate at 450 °C has two oxidation peaks and one reduction peak however the first oxidation peak at the potential -0.7(A₁) is not as defined as the first oxidation peak at -0.7 V(A₁) when compared to the manganese film annealed at 350°C on nickel. The second oxidation peak compared to the nickel 350°C film shows a broader peak and subsequently leads to the onset of oxygen evolution. The oxidation peaks of the 600°C on the nickel substrate exhibit two oxidation peaks also at the potentials of -0.7 V(A₁), which is smaller compared to the nickel 350°C and 450°C, and a sharp second oxidation peak at 0.45 V(A₂) and one sharp reduction peak at 0.35 V(C₁). The nickel substrate manganese films all exhibit oxidation and reduction peaks at the same potential however the intensity of the peaks vary with increasing annealing temperature.

In contrast to the manganese oxide film on nickel, the voltammetric responses of the manganese oxide films prepared on the titanium substrate contain less voltammetric characteristics. Another observation is that the titanium oxidation and reduction peaks vary with the change in annealing temperature. The manganese films on titanium at 350°C exhibits one oxidation peak at a potential of -0.3 V(A₁). As well as one reduction peak at the potential of -0.7 V(C₁), the manganese film on titanium at 450°C also exhibits this reduction peak at -0.7 V(C₁) however the intensity of the peak has decreased, while at an annealing temperature of 600°C there is no reduction peak at -0.7 V. The manganese film on titanium at 450°C and 600°C contain no oxidation peaks. As the annealing temperature of the manganese films on titanium increases, the intensity of the peaks decreases, outlined in figure 2(b)(d)(f) .

The overall reactions occurring in base between the manganese oxides are rather difficult to interpret. Manganese oxides are widely known to be rather complex and the assignment of the specific manganese species is difficult due to the wide range of oxidation states available for manganese (13). However, we propose the following redox reactions could be taking place between the manganese metal and hydroxide ions at the lower potential of -0.7 V:

Due to the production of the MnO or the manganous hydroxide at the first anodic peak, we suggest that at the second anodic peak the following two intermediate reactions may occur either separately or in unison to produce manganic oxide ;

1. Formation of a mixed oxide intermediate

2. Formation of a hydroxide intermediate

Furthermore the voltammetric response of the nickel substrate manganese oxide films (figure 2(a)(c)(e)) exhibits the onset of oxygen evolution at a potential of ca. 0.7V. During the oxygen evolution reaction various redox reactions may occur, we propose the following may take place;

During oxygen evolution the manganese dioxide may interact with the hydroxide ions in the solution to produce manganate ions or permanganate ions

Image 1: SEM of 350°C nickel electrode

Image 2: SEM of 350°C titanium electrode

When observing the SEM images, image 1 shows the surface morphology of the Mn_xO_y on the nickel substrate while image 2 shows the surface morphology of the Mn_xO_y on the titanium substrate. Image 1 contains a flakey morphology which appears to cover the surface of the electrode however redox peaks in the cyclic voltammetry, figure 2(a)(c)(e) resembles some of the characteristics of typical hydrous and electrodeposited nickel. However, this simply may be due to cyclic voltammetry being a very powerful analytical tool which has a low detection limit but the accuracy of identification of an analyte is not precise unless the exact analyte is known under known conditions (i.e.

Mn_2O_3 under ideal conditions) therefore other techniques, such as EDX or X-ray photoelectron spectroscopy(XPS), need to be explored to determine the compound formed on the surface of the electrode from the different annealing conditions. EDX analysis is discussed in this communication. However, XPS, which can determine the oxidation state of the various oxide, is not discussed in this communication but will be pursued as a route of analysis for future work on the manganese oxides. The titanium substrate Mn_xO_y electrode exhibits a cracked morphology with wave or ripple like surface. The difference in the morphology of the nickel and titanium substrate Mn_xO_y electrodes could indeed play a significant role in the difference in the Tafel analysis conducted on the different electrodes, figure 4(a)(b).

The voltammetric response for the nickel substrate Mn_xO_y electrodes, figure 2(a)(c)(e), is very similar to the hydrous and electrodeposited nickel electrodes which are also researched in this group. The similarities include both of these electrodes have one distinct anodic peak but the nickel substrate Mn_xO_y electrode has one distinct cathodic peak while the hydrous and electrodeposited nickel usually exhibit two cathodic peaks at potentials close to ca. 0.3 V and 0.4 V while the nickel substrate Mn_xO_y electrodes exhibits only one distinct sharp cathodic peak can be observed at a potential close to 0.4 V. To determine the elements involved in the voltammetric response SEM-EDX was used.

Image 3: SEM of 350°C nickel electrode

Figure 3: EDX of 350°C nickel electrode

The nickel substrate Mn_xO_y electrodes were characterized using SEM-EDX analysis to determine the elemental analysis of the nickel 350°C electrode, shown on image 3 and figure 3 above. The EDX results reveal the presence of manganese, oxygen and nickel. The large peak just before 1 keV shows that the manganese and oxygen are present in a much larger quantity than the nickel, which can be seen at about 7.5 keV therefore the voltammetric response shown in figure 2(a)(c)(e) could indeed be the voltammetric response of the manganese oxide and not nickel as it does not contain the full voltammetric characteristics of nickel. Similar voltammetric responses for manganese oxides in base have been reported in literature also (14, 15). From the literature it is also important to note that the voltammetric response for manganese oxides largely depend on the underlying metal support (15). Other manganese peaks can also be observed at 6 keV and 6.5 keV on the EDX graph. Another interesting feature in the voltammetric

characteristics of the nickel substrate Mn_xO_y electrode is that a hysteresis effect that is observed at the beginning of the hydrogen evolution reaction at a potential close to -1.2 V, seen in figure 2(a)(c)(e). The voltammetric response shows a unique crossover between the forward and backwards scans which is not seen on a voltammetric response of a hydrous or electrodeposited nickel.

OER kinetics and mechanism

In this section the typical steady state polarization curves of the Mn_xO_y electrodes on the titanium and nickel substrates at the annealing temperatures of 350°C, 450°C and 600°C in 1M NaOH base are compared, figure 5(a)(b). Tafel analysis of a system can be very useful to help and determine mechanistic information of the oxygen evolution reaction through calculating Tafel slopes, which help indicate if various kinetic steps in the reaction are determined by a chemical or an electron transfer steps and can also provide information relating to possible rate determining steps (RDS) for a multistep reaction. To obtain the tafel slopes of a multistep reaction and therefore obtaining the reaction order through the analysis of the steady state polarization curves done as a function of base concentration. The Tafel equation can be arrived following an approach by Bockris and Matthews. A multistep reaction may be considered from the following;

Where $\vec{n}$ is the number of electrons transferred before the RDS and n_r is the number of electrons transferred after the RDS. $\vec{n}$ can take a value between 0 and 1. If $\vec{n}$ takes a value of 0 and n_r takes a value of 1 then this indicates a chemical step prior to the rate determining step predicting a tafel slope of ca. 60mV dec⁻¹ at 25°C. If $\vec{n}$ takes a value of 0 and n_r takes a value of 1 with $\alpha = \beta = \frac{1}{2}$ then this indicates a first electron transfer step prior to the rate determining step which predicts a tafel slope of ca. 120mV dec⁻¹. Similarly when $\vec{n}$ takes a value of 1 and n_r takes a value of 1 with $\alpha = \frac{3}{2}$ this indicates a tafel slope of ca. 40mV dec⁻¹. Thus, the elucidation of Tafel slopes can be useful in determining possible reaction mechanisms (4).

If the assumption is made that all the steps in the multistep reaction can be described by the simple Butler-Volmer equation and that all the steps before and after the RDS are

in a state of quasi-equilibrium then the following, more general, Butler-Volmer equation for a consecutive multi-step reaction can be given by;

$$i = i_o \left\{ \exp \left[\left(\frac{\vec{n}}{v} + n_r \beta \right) \frac{F\eta}{RT} \right] - \left\{ \exp \left[\left(\frac{\vec{n}}{v} + n_r \beta \right) \frac{F\eta}{RT} \right] \right\} \right\} \quad [17]$$

Where i is the current density, i_o is the exchange current density, η is the overpotential and R, F and T have their usual meanings. We can define $\vec{\alpha} = \frac{\vec{n}}{v} + n_r \beta$ and $\tilde{\alpha} = \frac{\vec{\alpha}}{v} (1 - \beta) n_r$. When is the symmetry factor, generally taken to be 1/2, which arises from the activation of vibrational states and the energy required to break bonds. v is the stoichiometric number defined as the number of times the RDS occurs for one repetition of the overall reaction; therefore the Butler-Volmer equation can be simplified to;

$$i = i_o \left\{ \exp \left[\frac{\vec{\alpha} F \eta}{RT} \right] \right\} - \left\{ \exp \left[\frac{\tilde{\alpha} F \eta}{RT} \right] \right\} \quad [18]$$

which describes the net current for a redox couple. Taking for only an oxidation process, the Butler-Volmer equation can be written as;

$$i = i_o \left\{ \exp \left[\frac{\vec{\alpha} F \eta}{RT} \right] \right\} \quad [19]$$

Finally removing the ln from both sides of the equation the following Tafel equation is given;

$$\ln \frac{i}{i_o} = \frac{\alpha F \eta}{RT} \quad [20]$$

Therefore, a plot of the overpotential (η) vs log current (i) can be constructed and the Tafel slope, b , can be obtained from $2.303RT/\alpha F$. Tafel analysis assumes steady state therefore the polarization curves are carried out at a scan rate of 1 mV s^{-1} .

It is evident from these curves that the annealing temperature and substrate have an effect on the current recorded at a particular potential, therefore the lower Tafel region of each electrode will be different resulting in different Tafel slope values. When comparing the two substrates, titanium and nickel, it is evident from the graphs that the nickel substrate provided the Mn_xO_y system with the greater ability to provide lower overpotentials and higher log current values when compared to the titanium substrate. To better understand this substrate effect, the ohmic resistance of the electrochemical cell was measured using two different techniques: the built in CH iR test function and electrochemical impedance spectroscopy. Taking the Mn_xO_y titanium annealed at 450°C film as an example, the built in CH iR test was performed in a potential region with no observable faradaic activity and a solution resistance value of $10.3 \, \Omega$ was obtained. However, electrochemical impedance spectroscopy performed at the same potential suggests that the solution resistance is $3.9 \, \Omega$. This value was obtained from the high frequency resistive plateau in Figure 4 and is in line with typical values determined in 1.0 M NaOH solutions for standard metal electrodes. The discrepancy between these values suggests that an added resistance with a magnitude of ca. $6.4 \, \Omega$ is being measured by the

CH iR test function. This is possibly due to the formation of a thin passive oxide layer on the titanium substrate, giving it semi-conductor properties.

Figure 4: Electrochemical impedance spectrum recorded in the double layer region (-0.1V) for the Mn_xO_y titanium film at 450°C annealing temperature in 1 M NaOH represented in the bode-modulus format.

The tafel slopes for the nickel substrate Mn_xO_y vary between 180 mV dec^{-1} , 230 mV dec^{-1} and 330 mV dec^{-1} while the tafel slopes for the titanium substrate Mn_xO_y vary between 444 mV dec^{-1} , 1142 mV dec^{-1} and 3636 mV dec^{-1} for the electrodes that were annealed at 350°C, 450°C and 600°C respectfully.

Figure 5:(a) Comparison of Tafel Plots for thermally prepared Mn_xO_y on a nickel substrate in 1.0 M NaOH at a sweep rate of 1 mVs^{-1} , (b) Comparison of Tafel Plots for thermally prepared Mn_xO_y on a titanium substrate in 1.0 M NaOH at a sweep rate of 100 mVs^{-1} .

From the series of tafel slopes in figure 4(a) and (b) and in table 3 it can be stated the nickel substrate provides greater support for the Mn_xO_y . The results presented also depict that the optimum temperature to anneal the Mn_xO_y electrodes at is 350 degrees, as the current increases at a given potential as the annealing temperature of the electrodes decrease, therefore for the reaction order studies the Mn_xO_y electrode at the annealing temperature of 350°C on the nickel substrate was chosen. The titanium Mn_xO_y electrodes exhibit a large decrease in the initial onset in the OER overpotential with increasing annealing temperature. This could be due to the insulating properties of the titanium support. Literature shows that these oxide type electrodes on a titanium support can

exhibit a ‘mud cracked’ structure which allows the titanium metal to interact in the OER mechanism causing an insulating barrier effect thus causing an increase in the electrodes overpotential (5, 16). Perhaps with increasing annealing temperature, the Mn_xO_y paste on the titanium support becomes more ‘mud cracked’ allowing for a greater surface area of the titanium metal exposed. Which increases the interaction of the titanium support therefore increases the barrier effect causing the initial overpotential of the OER to increase, which can be observed in figure 5. Further SEM analysis will be done to confirm the surface structure on titanium support with the various annealing temperatures.

Figure 6: Comparing substrate and annealing temperature

Open circuit potential (OCP) decay curves were used in this work as well as steady state measurements to help determine the kinetics and mechanism of the Mn_xO_y electrode in alkaline solutions. Another reason we decided to use OCP analysis was due to the tafel slopes from the steady state analysis being very high. OCP analysis is a very useful technique to employ on metal electrode systems which may undergo alteration on the surface of the electrode over time in strong alkaline solutions.

In this work, OCP analysis is carried out by pre-polarizing the electrode at a potential in the Oxygen Evolution region therefore the electrodes were pre-polarised at a potential of 0.8V for a period of time to allow for the system to reach a steady current state. The time allowed for the system to reach steady current depends on the sample. However once a steady current state is achieved then the polarization is switched off and the potential is allowed decay with respect to time and lower and higher tafel slopes can be calculated for the decayed curve.

The tafel slope from the open circuit potential decay curves are calculated under the basis that the slope $-b_{\text{OCP}}$ from the E vs. $\log t$ decay curve is equal to the slope b of the tafel plot for the steady state polarization (4). In general the current density at the electrode can be written as the sum of the charging current (i_c) and the Faradic current (i_f);

$$i = i_c + i_f \quad [21]$$

At time t_o when the current is switched off, $i = 0$ and $\eta = \eta_0$ hence,

$$i_c = -i_f \quad [22]$$

Noting that,

$$i_c dt = dq ; C = \frac{dq}{dV} = \frac{dq}{d\eta_t} \quad [23]$$

Where q is charge and C is capacitance, we can show that,

$$-i_f dt = dt = C d\eta_t \quad [24]$$

Under anodic conditions with $\eta_t > RT/F$,

$$-i_o e^{\beta\eta_t F/RT} dt = C d\eta_t \quad [25]$$

Rearranging and integrating gives,

$$\int_{t_o}^t i_o dt = \int_{\eta_o}^{\eta} C e^{-\beta\eta_t F/RT} d\eta_t \quad [26]$$

Now, for $t \gg t_o$ and $\eta_o \gg \eta$,

$$-i_o t = \frac{RT}{\beta F} e^{-\beta\eta_t F/RT} \quad [27]$$

And taking the logarithm gives,

$$\eta_t = \frac{2.303RT}{\beta F} \log\left(\frac{RT}{\beta F i_o}\right) - \frac{2.303RT}{\beta F} \log(t) \quad [28]$$

Thus, an equivalent Tafel slope can be determined from the slope of a plot of the measured potential or overpotential during the decay as a function of $\log t$. Typical tafel slope results from OCP analysis for Mn_xO_y films in 1M base can be seen below, figure 6 and table 2 and 3.

Figure 7: OCP decay curves pre-polarized at 0.8V for (a) nickel substrate and (b) titanium substrate for 8 different annealing temperatures in the range of 250°C to 600°C.

TABLE 2. : OCP tafel slopes on titanium substrate.

Annealing temperature (degrees)	Lower Tafel slope (mV dec-1)	Higher Tafel slope (mV dec-1)
600	35±2.1	75± 5
550	47.5±5.6	12 ±7.4
500	35±2.1	113±11.5
450	40±1.3	67±11.5
400	42.5±5.1	115± 8.2
350	35±3.3	83±2.9
300	40±3.2	168±2.9
250	42.5±1.7	165±8.7

TABLE 3. : OCP tafel slopes on nickel substrate.

Annealing temperature (degrees)	Lower Tafel slope (mV dec-1)	Higher tafel slopes (mV dec-1)
600	13± 2.9	60± 13.2
550	73± 2.9	110± 5.0
500	42.5± 3.5	175± 5.0
450	52± 5.8	90± 0.0
400	55± 2.9	178± 10.6
350	63.5± 3.6	109± 2.9
300	57.5± 2.5	100± 5.0
250	54± 3.81	113± 2.9

The difference in the tafel slopes from the OCP measurements and the steady state measurements may arise from the decrease in the concentration of surface* groups, the site of oxygen evolution, as they become reduced as part of the accompanying cathodic process in self-discharge . This relates to the work of Conway and Bourgault, (17) which proposes the relationship between the decay slope and the steady state Tafel slope could be used to determine the potential dependence of the surface capacity and the fractional surface coverage of adsorbed intermediates.

*Hydrated surface species which undergo that undergo rapid redox transformations involving the gain or loss of electrons. These hydrated surfaces are located near the surface of the film [4].

At high but not total coverage of intermediates, the surface capacity increases with decreasing potential. The decay slope is therefore given by;

$$b_{OCP} = \frac{b'b}{b'-b} \quad [29]$$

Where b' is some positive multiple or fraction of RT/F hence the OCP tafel slope is less than the steady state Tafel slope. Subsequently instead of relating the surface capacity to adsorbed intermediate, Conway and Bourgault, we relate the surface capacity to surface groups or concentration of charged surface. Due to the difference in the OCP slope and the steady state analysis slope it would indicate that the surface capacity changes between the two types of measurements therefore also suggesting that the number of surface groups also changes [4].

Reaction order studies- 350°C nickel

From the kinetic data shown above from the Tafel analysis and the Open Circuit Potential decay curves the Nickel substrate with Mn_xO_y was chosen to undergo reaction order studies as it showed the lowest Tafel slope on steady state analysis of 188 mV dec^{-1} also the OCP analysis showed a lower tafel slope of $63.5 \pm 3.6 \text{ mV dec}^{-1}$ and a higher tafel slope of $109 \pm 2.9 \text{ mV dec}^{-1}$. Steady state tafel plots (figure 6) were recorded as a function of NaOH base concentration over the range of 5M to 0.01M.

Figure 8: Typical Tafel plots for active oxygen evolution recorded for thermally prepared Mn_xO_y material on a nickel substrate as a function of base concentration (5m-0.01M).

The reaction order studies undergone in this research were analyzed from various potential regions along the active oxygen evolution reaction site and the corresponding log current value was obtained for varying base concentrations, for the 350°C Mn_xO_y electrode the potentials chosen to perform the series of reaction order studies are 0.73V,

0.75 V and 0.78 V. These results are present in the figures 7, 8 and 9 below. Interestingly there appears to be two slopes appearing within the reaction orders therefore two reaction orders were calculated; one corresponding to the lower base concentrations (0.01M-1M) and one corresponding to the higher base concentrations (2M-5M).

Three different Mn_xO_y electrodes were prepared and reaction order studies were performed using the same nickel wire sealed in glass. The reaction orders were calculated from the following formula;

$$m_{\text{OH}^-} = \frac{\delta \log i}{\delta \log a_{\text{OH}^-}} \quad [30]$$

Where i is current, a_{OH^-} is the activity of the hydroxyl ion and m_{OH^-} is the rate of reaction.

Figure 9: Typical reaction order with respect to oxygen evolution recorded for thermally prepared Mn_xO_y material on a nickel substrate (base concentrations (5M-0.01M)) at $E = 0.73\text{V}$, 0.75V and 0.78V .

From the reaction orders above it can be stated that the reaction order for the Mn_xO_y paste is 0.5 at the lower concentration values. From the errors calculated it suggests that this DSA type electrode is reproducible with the highest deviation between log current value is 0.1304 and the lowest deviation is 0.002.

Mechanism

The kinetic data obtained from the OCP analysis for the 350 °C nickel electrode show that the lower tafel slope region are close to 60 mV dec⁻¹ and the higher tafel slope region are close to 120mV dec⁻¹ which would indicate that the first step in the reaction mechanism is a chemical transfer step and the second step in the reaction mechanism is the first electron transfer step, with a reaction order of 0.5 at the lower base concentration regions. According to Trassatti *et al.* fractional reaction orders may be due to the build-up molecules at the surface interface as the molecules are transitioning between acid – base species with the interaction with protonated molecules (OH⁻) (18).

S= co-ordinately unsaturated Mn atom (surfaquo group)

Two equally possible kinetic pathways (19)

The mechanistic sequence above involves an octahedral geometric molecule consisting of a central manganese atom, also referred to as the surfaquo group(S). The surfaquo group is attached to five ligands and has one free orbital which are all separated by a 90° angle from each other. At the free orbital attached to the surfaquo group the mechanism proposed above is suspected to take place.

To determine the molecular structure of the Mn_xO_y powder annealed at 350°C a Fourier Transform Infrared Spectrum was obtained, shown in figure 9. In the fingerprint region of the spectrum, the peaks at 525cm⁻¹ and 694cm⁻¹ could arise from stretching vibrations of the Mn-O and Mn-O-Mn bonds from the Manganese metal center on the

octahedral structure to the oxygen ligands attached. The peaks at 3382cm^{-1} can be assigned to $-\text{OH}$ stretching vibration along with the peak assigned to 1635cm^{-1} (20).

The FTIR analysis suggests that the manganese compound formed, which is involved in the OER mechanism, is either MnO_2 or Mn_2O_3 . Further elemental analysis will have to be conducted to determine the manganese compound formed on the metal support. Subsequently there's a possibility the two of these manganese compounds are formed on the metal support.

Figure 10: FT-IR of the 350°C powder

Conclusion/future work

The voltammetric profile for the Mn_xO_y film is strongly dependent on the nature of substrate. The Mn_xO_y film on the nickel substrate exhibits a greatly improved OER performance with respect to oxygen evolution overpotential than the titanium substrate. The reaction orders of the Mn_xO_y on the nickel substrate at lower temperatures has exhibited lower tafel slopes and better voltammetric profiles than at higher annealing temperatures on nickel or at any annealing temperature on the titanium substrate. The reaction order of the Mn_xO_y film on nickel at 350 degrees is approximately 0.5 at lower base concentrations (1M-0.01M), figure 8, which shows good reproducibility. Future work with the Mn_xO_y system includes more FTIR analysis on the electrodes at the different temperatures and XRD studies to further determine the type and structure of the manganese compounds annealed at the various temperatures which are on a nickel or titanium substrate.

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