Electrochemical properties of earth abundant catalysts for efficient water electrolysis

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This thesis is presented for the degree of Doctor of Philosophy of Murdoch University

2016
I declare that this thesis is my own account of my research and contains as its main content work which has not previously been submitted for a degree at any tertiary education institution.

..............................

Dario Alejandro Delgado Aguilar

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Abstract

The hydrogen economy is attracting a great deal of attention from governments and major oil companies. Hydrogen is seen as a solution to the problems arising from the current unsustainable fossil fuel economy. Hydrogen generation can be done thermochemically, electrochemically and biochemically. Of all these options, hydrogen generation using renewable energy inputs to split water electrochemically into hydrogen and oxygen is potentially attractive on a commercial scale. Water electrolysis has two reactions happening simultaneously, the hydrogen and oxygen evolution reactions (i.e. HER and OER) from the cathode and anode respectively. Most of the relevant published work supports the use of platinum group metals for the HER and platinum group oxides for the OER. Platinum group materials are expensive thus a cheap substitute is needed. In this respect, lower cost substitutes (e.g., manganese dioxide, Raney cobalt and Raney nickel) were investigated possessing the following characteristics: (a) stable in the reaction environment; (b) environmentally friendly, (c) good catalytic activity and (d) earth abundant.

The catalytic activity of materials in general can be enhanced by modifying their geometric and electronic factors. In the case of manganese dioxide (MnO₂), the electronic factor has been modified by changing its crystalline structure and chemical composition through a range of additives. In the case of nickel and cobalt as raw materials, their geometric factor has been modified by increasing the surface areas with the use of Raney powders. The electrochemical characteristics of the above materials were investigated by subjecting them to linear voltammetry and electrochemical impedance spectroscopy. The materials were also characterized by physical techniques using X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and X-ray photoelectron spectroscopy (XPS) analyses.

The obtained electrochemical results revealed that the best overpotentials found for Raney Ni and Raney Co in alkaline HER were -190 mV and -270 mV (i.e. η₁₀₀ at 100 mA cm⁻²) respectively. The presence of Mo, Co and V as additives in the parent
γ type MnO₂ substantially improved the catalytic activity towards acid and alkaline OER. In particular, for acid OER the Co/Mo bimetallic addition to γ–MnO₂ resulted in 305 mV (at $\eta_{100}$) which is competitive to that of commercially available DSA® which is 341 mV (at $\eta_{100}$). The physico-chemical characterization of the material before and after electrochemical experiments confirmed the stability in aqueous media. The effectiveness of the modified Watts bath for the deposition of Raney cobalt and Raney nickel, has been established through overpotential curves. The presence of oxide species lowers the efficiency of the electrode which increases the overpotential for the HER on Raney based electrodes. A porous Raney surface type enhances the available area for the hydrogen evolution reaction to occur which increases its energy efficiency (i.e. $\eta_{100}$). Recommendations for further developmental work for such catalysts are made.
Papers published based on the results of this thesis

Peer-reviewed Publications


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Chapter 1

1 Introduction*

1.1 Hydrogen Economy

The term ‘hydrogen economy’ was first coined by Bockris and Triner in 1970\(^1\), and it has been seen as a solution to many of the problems arising from the current unsustainable fossil fuel economy. Important contributions such as those by Meadows\(^2\), Hubbert\(^3\) and others\(^4\), have supported the establishment of hydrogen as an alternative source of energy. In recent years, the idea of hydrogen becoming significant in the energy market has started to receive increased attention. The energy outlooks of the top oil companies: Exxon Mobil\(^5\), Shell\(^6\) and BP\(^7\), all suggest a more diversified future energy supply mix in which hydrogen participates to a greater extent.

Exxon Mobil and BP energy outlooks for 2030 mention emerging alternative sources of energy; for example BP comments that ‘the fastest growing fuels are renewables (including biofuels)’. On the other hand, Shell energy scenarios for 2050 show hydrogen fuel cell vehicles (FCVs) competing with battery electric vehicles. In fact, Shell gives an even chance of only one of those two main technologies being fully developed in the near future.

It is difficult to predict the future: oil has faced opposition in the past, before it eventually came to dominate the energy market. Large major energy companies do not see hydrogen as being a major fuel in the near future; however, because of hydrogen’s unique advantages, there are several institutions interested in the study of economies based on solar- and nuclear-generated hydrogen\textsuperscript{4, 8}. There is still a probability of hydrogen being part of the energy mix in the future, which justifies further research of this technology.

‘Hydrogen technology’ as opposed to the ‘hydrogen economy’ offers several options that could be combined with systems already in place so as to achieve a synergistic effect. As a fuel, hydrogen produces energy (\textit{i.e.} electrical, mechanical, heat), and water as by-product. Hydrogen could thus address both energy and fresh water supply issues. For example, remote areas where water is in short supply could benefit from this technology. An industrial complex, for instance, could adjust the use of its off-peak reserves to produce hydrogen, to be stored and sold later.

A hydrogen economy could bring several benefits\textsuperscript{1, 8}. In addition to covering electricity demand, it could positively influence other sectors of the economy such as chemical technology, metallurgy and refining, effluents, water, and transportation, as a pollution-free fuel. It could also be used to convert organic waste into methane and ethylene. Hydrogen is an energy carrier and its transportation over practical distances between source and point of use, is cheaper by pipelines than electrical power lines\textsuperscript{1}. However, public acceptance, high capital investment, and the high present cost of hydrogen with respect to existing fossil fuels are some of the barriers facing large-scale adoption of this technology.
1.2 World Energy Sector

In 2003, Professor Richard Smalley, a Nobel prize winner in chemistry, ranked the top ten challenges the world is facing as: (1) energy, (2) water, (3) food, (4) environment, (5) poverty, (6) terrorism & war, (7) disease, (8) education, (9) democracy, and (10) population increase. The reason that energy and water are the numbers (1) and (2), respectively is that they are interrelated: with abundant clean energy, fresh water could readily be produced. One clean source of energy is solar energy, which can, in principle, be used for the development of water electrolysis.

Fossil fuels currently represent a high proportion of the total world primary energy consumption, with the rest being provided by nuclear and other non-conventional or renewable sources of energy. Fig. 1-1 shows that over three quarters of the global energy production is provided by fossil fuels (i.e. oil, gas and coal). The main problems with fossil fuels are that they are non-renewable and are a major source of CO$_2$ emissions into the atmosphere. In an effort to decrease CO$_2$ emissions, most countries are developing covert and overt policies based on their natural resources. Such policies can open up many opportunities, for example, countries rich in solar energy could aim to develop renewable, which could be combined with hydrogen generation for transportation. A proven case is Iceland, which has important sources of geo-thermal energy, currently has a hydrogen generation plant which is powered by geo-thermal (supported by the Shell oil company).

The Kyoto protocol is another example, this protocol is an international environmental treaty with the goal of achieving reduced emissions of greenhouse
gases. These examples show how many countries are willing to substantially increase their renewable energy share. By doing it so, they recognize that there has to be a change in their current energy supply to make it less polluting and therefore more sustainable. These changes in the energy supply will provide opportunities for new sources of energy; this is important because if technologies like solar and wind increase their share in the energy supply, it will create a foundation for the emergence of a hydrogen economy.

Fig. 1-1 Global Energy Mix.

1.3 Hydrogen Production

Hydrogen can be prepared by thermochemical, electrochemical, and biochemical processes and examples are the action of steam on heated carbon, the decomposition of certain hydrocarbons with heat, thermolysis of water, water electrolysis, displacement from acids or bases by certain metals, anaerobic digestion, etc. Of all these methods, only water electrolysis is likely to be suitable for the large scale production of hydrogen.
The appropriate selection of the source of electricity to drive water electrolysis will be a combination of cost and other circumstances such as the population needs for water and energy in a specific area and what technology is available. For instance, tidal energy is produced in the ocean or along coast lines. A formula for the estimation of the total cost of production of electrolytic hydrogen has been published\(^1\)

\[
\text{Cost} = 229E_c + 80 \tag{1-1}
\]

where:

- \(E\): cell voltage (V)
- \(c\): cost of the kWh\(_e\) in US cents (1974 prices)

According to Eq. 1-1, it is important to decrease the cell voltage and find a cheap source of electricity. The cell voltage is composed of the overpotentials for the electrochemical reactions and the IR drop through the electrolyte. The current work is focused on the overpotentials required to drive the water electrolysis. The purpose of Eq. 1-1 is to show the main variables that determine the cost of producing hydrogen, rather than giving an exact estimate of its cost. The parameters of this equation depend on technology, operational costs, government subsidies, etc. For example, if the cost of the electrolyzer can be lowered\(^4\), this would change the parameters of Eq. 1-1.
1.3.1 Water Electrolysis

Water electrolysis involves the splitting of water into its elemental constituents, hydrogen (H₂) and oxygen (O₂). This electrochemical process is not spontaneous, it needs a source of electrical energy to drive it. Fig. 1-2 shows a scheme for an electrolytic cell for splitting (electrolyzing) water. Here, the electron-transfer reactions which occur at the cathode and anode simultaneously, produce hydrogen and oxygen, respectively, and are driven endergonically by an outside source of electrical power.

Fuel cell technology uses the spontaneous direction of the water formation reaction to produce energy, with water as a by-product. Eq. 1-2 shows the reaction of water formation in the spontaneous direction.

\[ 2H₂ + O₂ \rightarrow 2H₂O \]  

Fig. 1-2 Driven Cell or Substance Producer⁹.
The two half-cell reactions of water electrolysis that occur at the surfaces of the electrodes and the overall reaction are shown in Table 1-1.

Table 1-1 Overall and Half Cell Reactions of Water Electrolysis.

<table>
<thead>
<tr>
<th>Half cell reactions</th>
<th>Acid solution</th>
<th>Alkaline solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathodic</td>
<td>2H⁺ + 2e⁻ → H₂(g)</td>
<td>2H₂O + 2e⁻ → 2OH⁻ + H₂(g)</td>
</tr>
<tr>
<td>Anodic</td>
<td>2H₂O → O₂(g) + 4H⁺ + 4e⁻</td>
<td>4OH⁻ → 2H₂O + 4e⁻ + O₂(g)</td>
</tr>
<tr>
<td>Overall</td>
<td>2H₂O(liq) → 2H₂(g) + O₂(g)</td>
<td></td>
</tr>
</tbody>
</table>

1.3.2 Sources of Energy for Electrolysis

The main sources of energy used to drive water electrolysis are solar and nuclear power⁴, ⁸. Energy sources that might be cost-effective in the future for water electrolysis are: photobiological, photochemical and thin-film solar processes, with wind energy as the last option⁴. In addition, Australian Government bodies forecast¹⁰ the use of tidal energy and geothermal hot dry rock for hydrogen generation. Nuclear-generated hydrogen is also a valid approach, but the use of such a technology is controversial.

Off-peak energy from conventional power plants is less controversial, especially in the hypothetical case where viable CO₂ sequestration is available. Unfortunately, American Government bodies mention neither tidal nor geothermal for hydrogen generation⁴. Non-conventional sources of energy in general are becoming more cost competitive. In particular solar power is forecast to cost ~0.1 US / kWh from a 500 kW photovoltaic plant by the year of 2020¹¹, which is very attractive given the current prices of fossil fuels. One figure that supports the use of solar in Western
Australia is based on the assumption that with an extraction efficiency of 25%, the deserts of western and central of Australia could yield as much as 194,000,000 GWhe / year\(^1\).\(^{12}\) (698.4 EJ/year).

Electricity from coal is by far the cheapest option ranging AUD (2006) 27 to 37/MWh\(^1\(^3\) but negative externalities such as CO\(_2\) emissions, acid rain source, etc, have not been included and the cost of CO\(_2\) geosequestration has not been assessed. In Australia, progress on this respect has been done; on the 1st of July 2012 the Australian Federal government introduced carbon taxing\(^1\(^4\). The carbon tax was initially fixed at 23 AUD/ tonne of emitted CO\(_2\) equivalent. Hence, the appropriate selection of the source of energy should be made based on Eq. 1-1.

1.4 Research Objective

Catalysts for chemical reactions belong, in general, to the platinum group. Platinum group elements are scarce resources and thus expensive. Substitutes for these materials should be earth-abundant. Electrodes for hydrogen and oxygen evolution are developed for acid and alkaline media. An electrode becomes a catalyst when it is competitive in terms of reaction overpotential. The initial raw material selection for electrode development is based on cost, earth-abundance and a certain degree of electrolytic activity.

The approach to make cost efficient and efficient catalysts is by improving their geometric and electronic factors. Increasing the roughness factor or surface area, by the use of porous surfaces, is the most common technique for geometric factor enhancement. Comparatively, improving the electronic factor is difficult to achieve;
however, adding Co and Mo as dopants to MnO$_2$ resulted in better performance. In addition, the role of modified Watts bath for the deposition of Raney cobalt and Raney nickel has also been extensively studied in this thesis.

### 1.5 References


Chapter 2

2 Literature Review

2.1 Water Electrolysis Fundamentals*

In section 1.3, the cell voltage and overall water electrolysis reaction terms were introduced. Eq. 2-1 shows what variables compose the cell voltage for a electrochemical reaction which for our case is water electrolysis. Variables which can be technologically improved are the overpotentials and Ohmic potential drop.

The cell voltage for a driven cell is defined as¹:

\[ E = E_\text{e} + \eta_\text{a} - \eta_\text{c} + IR \]  

where:

- \( E_\text{e} \): Equilibrium cell potential (V).
- \( \eta_\text{a} \) and \( \eta_\text{c} \): overpotential at the cathode or anode, respectively (V).
- \( IR \): Ohmic potential drop in the electrolyte (V).

At standard conditions of temperature and pressure (\( T = 298 \) K (25 °C), \( P^0 = 1 \) bar), water is liquid, while hydrogen and oxygen are gaseous. The changes in the standard Gibbs energy \( \Delta G^0 \), enthalpy \( \Delta H^0 \), and entropy \( \Delta S^0 \), accompanying the

dissociation of water (i.e. the reverse of the formation of water) correspond to the thermodynamically reversible (i.e. equilibrium) electrolysis potential for water $E_e^o$ and they are:

\[
\begin{align*}
\Delta G^o &= 237.22 \text{ kJ mol}^{-1} \\
\Delta H^o &= 285.84 \text{ kJ mol}^{-1} \\
\Delta S^o &= 163.15 \text{ J mol}^{-1} \text{ K}^{-1} \\
E_e^o &= 1.229 \text{ V}
\end{align*}
\]

At equilibrium, the cathodic and anodic current densities at the electrode are equal in magnitude and opposite in direction; this is called the exchange current density ($i_o$). The equation to determine the equilibrium potential at conditions different to those from the standard is the Nernst equation. The Nernst Eq. in its half-cell reduction potential form is shown as Eq. 2-2,

\[
E_{\text{red}} = E_{\text{red}}^o - \frac{R}{zF} \ln \frac{a_{\text{red}}}{a_{\text{ox}}} \tag{2-2}
\]

where:

$E_{\text{red}}$: half-cell reduction equilibrium potential (V).

$E_{\text{red}}^o$: half-cell standard reduction potential (V).

$R$: universal gas constant (8.3144 J K$^{-1}$ mol$^{-1}$).

$T$: absolute temperature (K).

$z$: number of moles of electrons transferred in the half-cell reaction.

$F$: Faraday constant 96,485 (C mol$^{-1}$).
$a_{\text{red}}, a_{\text{ox}}$: a is the chemical activity for the involved species, where $a_{\text{red}}$ is the reductant and $a_{\text{ox}}$ is the oxidant. $a_i = \gamma_i c_i$, where $\gamma_i$ is the activity coefficient and $c_i$ the concentration of species $i$.

The minimum energy that the power supply must deliver for the overall water electrolysis reaction to happen is the Gibbs energy change of the water dissociation reaction ($\Delta G_d \text{kJ mol}^{-1}$):

$$\Delta G_d = -n F E_e$$  \hspace{1cm} 2-3$$

where:

$n$: number of electrons exchanged during the electrochemical splitting of water

$(n = 2$, dimensionless$)$. 

$E_e$: water equilibrium potential (V) ($cf.$ Eq. 2-1$)$. 

The value of $\Delta G_d^0$ includes the energy provided from the environment as heat by the $T\Delta S_d^0$ term ($cf.$ Eq. 2-5$)$. In the hypothetical case that no heat were available from the environment, then the energy required to split water would increase. The heat ($T\Delta S_d^0$) provided from the environment at the standard condition divided by $2F$ represents 0.25 V, therefore without this extra source of energy, the thermodynamic electrolysis voltage would increase to approximately 1.48 V. This is called the thermo-neutral potential at which heat is neither being taken from the surroundings to create hydrogen, nor rejected to the surroundings. Under this condition the electrolysis is carried out entirely by electricity$^2$ and this potential is used as a
reference to run the electrolysis. Above this potential, heat is given out as excess (i.e. there are energy losses). Eq. 2-4 defines the thermo-neutral potential:

\[ E = \frac{\Delta H}{nF} \]  

The Gibbs energy change of the water dissociation reaction is a function of the operating temperature and pressure, as shown in Eq. 2-5:

\[ \Delta G_d = \Delta H_d - T\Delta S_d > 0 \]  

Another important condition for water electrolysis is the pressure; the selection of the operating pressure is based on costs. The higher the pressure the hydrogen is produced, the better, because energy and money can be saved by removing the need for a compressor. The recommended operating pressure for water electrolysis is 2,000 psi (13.8 MPa)\textsuperscript{2a}, it should be mentioned that even higher pressures have been researched, for example, ultrahigh-pressure electrolysis operating at 5,000 –10,000 psi (34.5–68.9 MPa)\textsuperscript{3}. Similarly, the current density is also determined by costs: the higher the current density, the higher the energy losses and operational costs. A current density of about 100 mA cm\textsuperscript{-2} appears to be economically optimal\textsuperscript{2b}.

Another important component of water electrolysis is the membrane which selectively permits the flow of hydrogen ions produced at the anode to the cathode where they are reduced to molecular hydrogen. During electrolysis, liquid water is
consumed at the anode but water from the cathode migrates to the anode by a process known as electro-osmosis. The membrane material mostly used is Nafion\textsuperscript{2a}. This material is extensively used for the development of proton exchange membrane (PEM) cells.

Thermodynamics determine the conditions for the water electrolysis to occur. In this respect, there is a variable called thermo-neutral potential (Eq. 2-4) and at standard conditions this potential would be 1.48 V as previously discussed. To conclude, one has to take special attention to the catalysts (i.e. cathode and anode surfaces), where the H\textsubscript{2} and O\textsubscript{2} are produced. The catalysts determine the overpotential of the electrolysis, which constitutes a high proportion of its cost (cf. Eqs. 1-1 and 2-1). Overpotential in water electrolysis is the difference between the thermodynamic potential and the potential that is needed to drive the reaction at an appropriate rate (Eq. 2-6).

\[ \eta = a - b \log i \]  

where:

\( \eta \): overpotential (mV).
\( a \): constant (mV).
\( b \): 2.303 \( RT/\beta F \) (Tafel’s equation).
\( i \): current density (mA cm\textsuperscript{-2}).

### 2.2 Reaction Mechanisms of Water Electrolysis

Why bother about determining a mechanism? The overall electrochemical process is a combination of two half-cell reactions. A common error found in
industrial laboratories is excessive focus on the overall reaction. In order to make progress one should look in detail at the individual reactions at the electrodes.

To minimize the energy and hence economic cost losses caused by overpotential, it is essential to know the rate-determining step (rds) in the reaction sequence. This offers the best possibilities on improving catalytic surfaces. Various electrochemical approaches in combination with the reaction pathway help to determine the rds; for example, a systematic use of the Tafel equation can be used to establish the rds.

Water electrolysis includes the hydrogen and oxygen evolution reactions. However, the chlorine evolution reaction has to be considered because this reaction competes with oxygen evolution in seawater electrolysis. Saline and alkaline waters require different types of anodes (i.e. water oxidizer electrode). In saline-water electrolysis, chloride ions are oxidized at the electrode surface producing gaseous chlorine which is corrosive and harmful. Therefore, selective electrodes that produce oxygen over chlorine should be used. This is not the case for alkaline water electrolysis, where oxygen is the only product being generated, requiring no selective electrodes. We have included the chlorine evolution mechanism to have a broader view of about mechanisms and other catalysts that have been tried.

2.2.1 Hydrogen Evolution Reaction (HER)

Electrochemical reactions in general behave differently under acidic and basic conditions. Water electrolysis under practical conditions keeps the solution in the cathode compartment (i.e. catholyte) basic and the solution in the anode compartment (i.e. anolyte) acidic. The hydrogen evolution reaction mechanism has
three distinguishable steps\(^1,4\) as shown in Table 2-1.

Table 2-1 HER Path Mechanism in Acid and Alkaline Solutions.

<table>
<thead>
<tr>
<th>Step name</th>
<th>Acid solution</th>
<th>Alkaline solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrochemical/Charge transfer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>steps:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volmer/Hydrogen adsorption/Proton</td>
<td>(M + H_3O^+ + e^- \rightleftharpoons M - H + H_2O)</td>
<td>(M + H_2O + e^- \rightleftharpoons M - H + OH^-)</td>
</tr>
<tr>
<td>Heyrovsky/</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrochemical desorption by recombination path</td>
<td>(M - H + H_3O^+ + e^- \rightleftharpoons H_2 + H_2O + M)</td>
<td>(M - H + H_2O + e^- \rightleftharpoons H_2 + OH^- + M)</td>
</tr>
<tr>
<td>Chemical step:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tafel/Catalytic path</td>
<td>(M - H + M - H \rightleftharpoons H_2 + 2M)</td>
<td>(M - H + M - H \rightleftharpoons H_2 + 2M)</td>
</tr>
</tbody>
</table>

In the reaction steps shown in Table 2-1, “M” stands for the participating active-site atom (i.e. not only a metal atom) from the electro-catalyst. The desorption and catalytic paths are two alternatives for the evolution of gaseous hydrogen, which may occur along either, depending on the electrode. The HER path mechanism can be reasoned with the Tafel slope, which indicates the rds, for example a slope of \(2RT/F\) indicates that the rds is proton discharge. A Tafel slope analysis is appropriate but not sufficient, other tests are required to determine the mechanism\(^1,5\).

2.2.2 Oxygen Evolution Reaction (OER)

Models for the OER are still being developed; there are several proposed paths which fit all the constraints. For instance, different ideas have been proposed for reactions happening in the double layer interface (as opposed to the catalyst surface)\(^6\). Certainly the OER mechanism appears to be more complicated than that of the HER. Table 2-2 contains the various pathways for oxygen evolution on metal oxides that are consistent with electrochemical observations.
Recent publications\(^7\) show different OER mechanisms than the ones shown in Table 2-2. A mechanism can be developed by the combination of kinetic or thermodynamic tools, the former approach in general gives more accurate results, however narrowing down possible paths is done by the aid of the latter.

<table>
<thead>
<tr>
<th>Acid solution</th>
<th>2) Oxide path(^9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Electrochemical oxide path(^9)</td>
<td>2) Oxide path(^9)</td>
</tr>
<tr>
<td>a) ( M + H_2O \rightarrow M - OH + H^+ + e^- )</td>
<td>a) ( M + H_2O \rightarrow M - OH + H^+ + e^- )</td>
</tr>
<tr>
<td>b) ( M - OH \rightarrow M - O + H^+ + e^- )</td>
<td>b) ( 2M - OH \rightarrow M - O + M + H_2O )</td>
</tr>
<tr>
<td>c) ( 2M - O \rightarrow 2M + O_2 )</td>
<td>c) ( 2M - O \rightarrow 2M + O_2 )</td>
</tr>
<tr>
<td>3) Krasil’shchkov path(^10)</td>
<td>4) Wade and Hackerman’s path(^11)</td>
</tr>
<tr>
<td>a) ( M + H_2O \rightarrow M - OH + H^+ + e^- )</td>
<td>a) ( 2M + 2H_2O \rightarrow MO + MH_2O + 2H^+ + 2e^- )</td>
</tr>
<tr>
<td>b) ( M - OH \rightarrow M - O^- + H^+ )</td>
<td>b) ( MO + 2MOH^- \rightarrow 2M + MH_2O + O_2 + 2e^- )</td>
</tr>
<tr>
<td>c) ( M - O^- \rightarrow M - O + e^- )</td>
<td>c) ( 2M - O \rightarrow 2M + O_2 )</td>
</tr>
<tr>
<td>d) ( 2M - O \rightarrow 2M + O_2 )</td>
<td></td>
</tr>
<tr>
<td>5) Electrochemical oxide path(^9)</td>
<td>6) Oxide path(^9)</td>
</tr>
<tr>
<td>a) ( M + OH^- \rightarrow M - OH + e^- )</td>
<td>a) ( M + OH^- \rightarrow M - OH + e^- )</td>
</tr>
<tr>
<td>b) ( M - OH + OH^- \rightarrow M - O + H_2O + e^- )</td>
<td>b) ( 2M - OH \rightarrow M - O + M + H_2O )</td>
</tr>
<tr>
<td>c) ( 2M - O \rightarrow 2M + O_2 )</td>
<td>c) ( 2M - O \rightarrow 2M + O_2 )</td>
</tr>
<tr>
<td>7) Krasil’shchkov path(^10)</td>
<td>8) Yeager’s path(^12)</td>
</tr>
<tr>
<td>a) ( M + OH^- \rightarrow M - OH + e^- )</td>
<td>a) ( M + OH^- \rightarrow M - OH + e^- )</td>
</tr>
<tr>
<td>b) ( M - OH + OH^- \rightarrow M - O^- + H_2O )</td>
<td>b) ( M^2 - OH \rightarrow M^{2+} - OH + e^- )</td>
</tr>
<tr>
<td>c) ( M - O^- \rightarrow M - O + e^- )</td>
<td>c) ( 2M^{2+} - OH + 2OH^- \rightarrow 2M + 2H_2O + O_2 )</td>
</tr>
<tr>
<td>d) ( 2M - O \rightarrow 2M + O_2 )</td>
<td></td>
</tr>
<tr>
<td>9) Bockris’ path(^13)</td>
<td></td>
</tr>
<tr>
<td>a) ( M + OH^- \rightarrow M - OH + e^- )</td>
<td></td>
</tr>
<tr>
<td>b) ( MOH + OH^- \rightarrow M - H_2O_2 + e^- )</td>
<td></td>
</tr>
<tr>
<td>c) ( M - H_2O_2 + OH^- \rightarrow M - O_2H^- + H_2O )</td>
<td></td>
</tr>
<tr>
<td>d) ( M - H_2O_2 + M - O_2H^- \rightarrow H_2O + OH^- + O_2 )</td>
<td></td>
</tr>
</tbody>
</table>

**Table 2-2 Path Mechanisms of Oxygen Evolution on Metal Oxides\(^8\).**

“M” stands for the participating active site on the electro-catalyst, the others are standard chemical symbols.

Recent publications\(^7\) show different OER mechanisms than the ones shown in the previous Table 2-2.
This publication\textsuperscript{7} used a mechanistic approach to develop the previous mechanism. Why they have proposed a different mechanism than the ones shown in Table \textsuperscript{2-2}? They used a thermodynamic (i.e. thermo-mechanic) approach which probably benefits low energy profile intermediates, and the models from the Table \textsuperscript{2-2} are developed by an electrochemical approach (i.e. kinetic). It is well known that if a specie is thermodynamically favoured, it does not mean that it is kinetically dominant, and what it is important is whether the specie is kinetically dominant or not. Which mechanism or approach is the correct one?, there are several proposed OER mechanisms, there must be only one of those happening dominantly. It is difficult to develop a sound explanation which would result on a definitive OER mechanism. A mechanism mainly depends on catalyst material, electrostatic potential, electrolyte, temperature and pressure.

One example to show the complexity of finding an application for a proposed mechanism is found in the modification of MnO\textsubscript{2} to enhance its electrochemical activity\textsuperscript{14}. OER on MnO\textsubscript{2} has been reported to have a mechanism similar to that of Yeager’s (Table \textsuperscript{2-2})\textsuperscript{15}. Other publications have reported an onset of resonance tunnelling or mediation of the OER by higher oxidation states of the catalyst’s participating active site, generated by a M^z/M^{z+1} reversible redox reaction (i.e. resembling a Yeager path)\textsuperscript{6a, 16}. It is believed that means to stabilize the redox pair
$M^z/M^{z+1}$ could improve the OER catalytic properties of materials which show a Yeager path\textsuperscript{14}.

As an initial approach for stabilizing the $M^z/M^{z+1}$ pair in MnO\textsubscript{2} when used for the OER, could consider the theories for charge storage in MnO\textsubscript{2}\textsuperscript{17}. The first theory explains that proton (H\textsuperscript{+}) and alkali metal cations (C\textsuperscript{+}), present in the electrolyte, can be reversibly intercalated into the bulk of MnO\textsubscript{2} through a reduction reaction and deintercalated via an oxidation reaction:

\begin{align*}
\text{MnO}_2 + \text{H}^+ + e^- & \rightleftharpoons \text{MnOOH} \quad 2-11 \\
\text{MnO}_2 + \text{C}^+ + e^- & \rightleftharpoons \text{MnOOC} \quad 2-12 \\
\text{Mn}^{4+} + e^- & \rightleftharpoons \text{Mn}^{3+} \quad 2-13
\end{align*}

The second theory explains it, through surface electrosorption of cations on MnO\textsubscript{2}:

\begin{align*}
(\text{MnO}_2)_{\text{surface}} + \text{C}^+ + e^- & \rightleftharpoons (\text{MnO}_2^{-} \text{C}^+)_{\text{surface}} \quad 2-14 \\
(\text{Mn}^{4+} + e^- & \rightleftharpoons \text{Mn}^{3+}) \quad 2-15
\end{align*}

In both theories there is a reversible redox reaction between Mn\textsuperscript{4+} and Mn\textsuperscript{3+} to maintain electroneutrality. In both theories a cation is involved in the mechanism to generate the Mn\textsuperscript{4+}/Mn\textsuperscript{3+} pair. In this respect, divalent ion (e.g. Ni\textsuperscript{2+}, Mg\textsuperscript{2+}) doping has been examined to stabilize the Mn\textsuperscript{4+}/Mn\textsuperscript{3+} pair\textsuperscript{14} to improve the catalytic
properties of MnO\textsubscript{2}, as this pair is involved as mediator in oxygen reaction mechanisms. This reasoning shows how one could find an application to a proposed mechanism to improve the properties of a material, in this case for MnO\textsubscript{2}.

### 2.2.3 Chlorine Evolution Reaction (CER)

We are focused in developing electrodes for acid and alkaline water solutions. However, there is relevant work done in seawater electrolysis related to MnO\textsubscript{2}\textsuperscript{18}. We have included the CER mechanism to have a wider idea about proposed reaction mechanisms. Several mechanisms have been proposed for the CER based on electrochemical analyses\textsuperscript{19}:

**Volmer-Tafel reaction**

\[
2M + 2Cl^- \rightarrow 2Cl^- M + 2e^- \rightarrow 2M + Cl_2 + 2e^-
\]

\textsuperscript{2-16}

**Volmer-Heyvrosky reaction\textsuperscript{20}**

\[
M + 2Cl^- \rightarrow Cl^- M + e^- + Cl^- \rightarrow M + Cl_2 + 2e^-
\]

\textsuperscript{2-17}

**Khrishtalik reaction\textsuperscript{21}**

\[
M + 2Cl^- \rightarrow Cl^- M + e^- + Cl^- \rightarrow (Cl^- M)^+ + 2e^- + Cl^- \\
\rightarrow M + Cl_2 + 2e^-
\]

\textsuperscript{2-18}

The reaction mechanisms for chlorine evolution are still being formulated. This is especially in regard to what happens at the atomic scale, which is known to depend strongly on the catalyst material, the electrostatic potential, and the electrolyte. Under standard conditions, the equilibrium potentials for Cl\textsubscript{2} and O\textsubscript{2} evolution are
1.36 V and 1.23 V, respectively. However, depending on the catalyst, the overpotential for the OER could be either higher or lower than that of the CER\textsuperscript{7a}. In this respect, metal oxides always show a potential for the OER larger than that of the CER\textsuperscript{7a} as shown on Fig. 2-1 (i.e. a so called volcano plot for the CER).

A volcano plot is a useful tool for the analysis of different potential materials for catalyst. A volcano plot is created by plotting on the abscissa a function involving some property of the catalyst\textsuperscript{1}, e.g. heat of sublimation, inter-atomic distance among the surface atoms or the bond strength of the intermediate species with the catalyst and in the coordinate a variable which represents electrochemical activity. Fig. 2-1 shows the theoretical CER and OER volcano developed by density functional theory (DFT) (as well as Fig. 2-4). This Fig. illustrates the activity of some selected rutile oxides.

TiO\textsubscript{2} does not appear on this plot because its activity was found to be out of the scale (i.e. low activity). It should be noted that, the CER does not have the regular volcano shape (i.e. V shape), because at the studied conditions, there are different CER mechanisms competing with each other, giving a different than the usual volcano shape. However, the OER does have the usual volcano shape. Fig. 2-1 shows that most of the selected materials will produce chlorine preferentially over oxygen from a thermodynamic point of view.
Recent studies\textsuperscript{7a} show reaction mechanisms involving reactive oxygen species which are, in addition, OER intermediates, being involved in the CER. Intermediates such as ClOM, Cl(M)\textsubscript{2}, ClM, have been proposed where ‘M’ for this particular case is surface oxygen from one of the OER intermediates. The same publication\textsuperscript{7a} which had a quantum-mechanistic approach, mentions that Pt/MnO\textsubscript{2} catalyst in acid has an energy of 0.3 eV for oxygen evolution higher than the potential of chlorine evolution. This information is important for the development of oxygen selective electrodes for saline water.

![Theoretical Volcano Plot for the CER/OER of a few Selected Metal Oxides\textsuperscript{7a}.](image)

For Pt/MnO\textsubscript{2}, the potential for chlorine evolution is 0.4 V lower than that of the OER\textsuperscript{7a}. This contradicts experimental evidence of MnO\textsubscript{2} as a selective electrode for the OER over the CER in seawater. First of all, this result is based on a thermomechanistic approach; thermodynamic unknowns are filled in with the aid of quantum mechanics. This thermodynamic approach does not explain why oxygen evolution is the preferred product from MnO\textsubscript{2} based catalysts, in fact, it suggests the
opposite. However, a thermodynamic approach is important but not sufficient, what can be extracted is that definitely this material has some sort of selectivity towards either the OER or CER.

Limitations from a thermodynamic analysis on oxygen selective electrodes over chlorine evolution, are; a biased mechanism which not represents exactly the correct steps for gas evolution. Another limitation is computer chemistry, which is a field that is gaining more popularity as computing power increases, however this approach requires several approximations that could sometimes lead to wrong conclusions.

If thermodynamics fails to explain the experimental observation of MnO$_2$ favoring the production of O$_2$ over Cl$_2$ in seawater, what it is left is a kinetic approach. This analysis has been done for iridium based electrodes and found that in simultaneous OER and CER that$^{18a}$:

a. Chlorine evolution is a potential-controlled reaction limited by the number of active sites on the catalyst surface.
b. Oxygen evolution is surface-transport-controlled (a.k.a. surface diffusion controlled).

This kinetic approach might help to explain the selectivity for the OER on MnO$_2$-based electrodes. For instance, operating at higher temperatures improves the transport of oxygen intermediates along the catalyst surface, leaving less active sites for the CER. It is also well-known that higher temperatures increase the rate of reactions with higher energy of activation. This reasoning is supported by
publications involving MnO$_2$-based electrodes where temperature improves the OER selectivity.$^{18e}$

### 2.3 Catalysts for Water Electrolysis

In the context of water electrolysis, a catalyst (electrode) is a material that lowers the energy threshold for both, the hydrogen and oxygen evolution reactions. As such, it is a material that speeds up the electrochemical processes by allowing them to take place more easily, thereby lowering energy consumption, producing less waste and influencing product selectivity. In general, catalysts operate by lowering the activation energy ($\Delta G^\ddagger$) of a reaction (Fig. 2-2). This is achieved by stabilization of the transition state, destabilization of the reactants or by creating a new reaction path.

There are two equivalent equations that determine the energy of activation, the Arrhenius and the Eyring equations, also known as Eyring–Polanyi equation. Eqs. 2-19 and 2-20, respectively.

$$k = Ae^{\frac{E_a}{RT}}$$  \hspace{1cm} 2-19

$$k = \frac{k_B T}{h} e^{\frac{-\Delta G^\ddagger}{RT}}$$  \hspace{1cm} 2-20

where:

- $k$: rate constant of a chemical reaction (units depends on the reaction order).
- $A$: pre-exponential constant or frequency factor (units depends on the reaction order).
\( E_a \): activation energy (J mol\(^{-1}\)).

\( k_B \): Boltzmann constant (1.38 \times 10^{-23} \text{ J K}^{-1}).

\( h \): Planck’s constant (6.62 \times 10^{-34} \text{ J s}).

These Eqs. 2-19 and 2-20 also explain why it is beneficial to run reactions at higher temperatures. The rate constant \( k \) is a measure of the speed of a chemical reaction. Its dependence on temperature means that the higher the temperature, the faster the reaction. In addition, an increase of temperature lowers the equilibrium potential of a chemical reaction. This lowers the electrical power needed to drive the electrochemical reaction.

The Arrhenius equation is another approach to determine the rds. As shown on the Fig. 2-2, different reaction paths have different activation energies. Fig. 2-2 shows two mechanisms with different speeds and it can be seen that the path with the smaller Gibbs energy is more energy efficient.

![Fig. 2-2 The Reaction Coordinate and the Transition State.](image-url)
There are two recognized ways to improve the catalytic properties of an electrode\(^1\). The first is to alter the structure of the electrode surface to increase its roughness (geometric factor). The second is to enhance the ‘electronic factor’ of the electrode. This refers to the catalyst-intermediate bond strength which is also known as the Sabatier principle. The Sabatier principle states that the interactions between the catalyst and the intermediate species should be neither too strong nor too weak. In this respect, changes at the molecular level on the electrode are important for the development of more efficient electrodes or catalysts.

There are sound approaches for improving the geometric and electronic factors of catalysts (also known as size and intrinsic effects). Several articles have focused on the enhancement of the electronic factor, for example by using mixed metal oxides\(^{14, 22}\). While others have worked on the geometric factor, for instance with Raney nickel based electrodes\(^{23}\).

The influence of the geometric factor on an electrochemical reaction is straightforward, the greater the available area the more molecules can react for the same period of time. On the other hand, understanding the electronic factor requires knowledge of how the energy profile of the activated complex can be altered to make the electrochemical reaction happen at lower activation energies. The electronic factor is analyzed by computer chemistry, one example is the recent\(^ {24}\) deciphering of the mechanism of the oxygen evolving complex (OEC) for oxygen evolution on green plants (i.e. photosynthesis), this is an important finding towards the artificial production of hydrogen and oxygen. This process is known to be highly efficient and this is a step towards mimicking it.
A current novel trend for catalysts design is the combination at the molecular scale of elements which show low and high bond strength with the reaction intermediates to generate intermediate bond strength, which is where catalysts operate the best\textsuperscript{25}. For example, by looking at Fig. 2-3, one could test combinations of titanium and indium to find by interpolation a material with an intermediate M-H bond strength which would be more energy efficient than platinum group metals. There is a successful example by using this approach. In the design for catalysts for ammonia synthesis, the combination of Co/Mo has been theoretically-experimentally reconciled and found to outperform ruthenium (i.e. platinum group element)\textsuperscript{25}.

At present, most electrode catalysis research, relevant to improving hydrogen technology, specifically for water electrolysis, includes\textsuperscript{3}; (a) more active electrodes at low temperature; (b) cheaper electrodes using less noble metals and (c) multifunctional catalysts. However, there are fundamental issues that need clarification regarding the efficiency of catalysts in general\textsuperscript{3}:

- Understanding catalytic activity from one system to the next;
- Understanding selectivity and trends in selectivity (i.e. preferential reactions);
- Understanding deactivation mechanisms (i.e. catalyst poisoning);
- Defining and understanding the chemical and structural state of the active site during catalysis (computer chemistry);
- Understanding the size effects in catalysts;
- Understanding metal-metal interaction in bi- and multi-metallic catalysis; and
- Finding ways to produce novel micro- and mesoporous solids (i.e. catalyst’s geometric factor enhancement).

### 2.3.1 HER Catalyst Materials

Materials such as the platinum group metals: platinum, rhodium, iridium, rhenium, ruthenium and to some extent gold are the best elements for the HER as shown in “volcano-type” plots\(^1\). Fig. 2-3 shows the best pure metals (i.e. not alloys) for the HER. These metals have both a high exchange current density (a measure of catalyst activity) and intermediate metal-hydrogen bond strength. However, the platinum group metals are extremely expensive, particularly for industrial scale application.

![Experimental Volcano Plot for Hydrogen Evolution Reaction on Metal Surfaces\(^1\)](image)

Platinum is the most widely used material as a catalyst because of its stability, availability and catalytic power. Other noble metals (except for gold) are less readily
available in wire or plate forms. These are expensive materials, however an inexpensive metal could be substantially enhanced, as say for example, lead when used as lead dioxide PbO₂ also known as ‘the poor man’s platinum’ but lead is carcinogenic and the technology concept should be environmentally friendly, economic and socially acceptable.

The volcano plot for the HER (Fig. 2-3) shows a group of elements which have catalytic properties close to that of the platinum group. This running up group includes iron, copper, cobalt²²a (not shown), and nickel. Nickel is chemically stable for this purpose and from this point of view, it can be seen that nickel would be a the best approach.

Nickel has been selected for this PhD project as the main component for the HER electrode material. Note that, there are highly specialized electrolyzers which operate at either low or high pressure using Ni-based electrodes²⁶. As mentioned previously, Raney-Ni is a sound option and it is believed that its electronic factor could be improved by adding other transition elements. This material concept would lie on the category of electrodes based on Raney-Ni. Raney Nickel has a good geometric factor, by adding a sound combination of other elements is possible to improve its electronic factor. Raney cobalt has also been selected for this research, this material in particular has been substantially less studied for the HER. In this respect, these materials would lead to a positive outcome while testing new materials for the HER.

2.3.2 OER Catalyst Materials

Non-platinum and platinum electrocatalytic systems have been widely studied²²a.
and have been grouped into what has been called the hypo-hyper $d$-intermetallic electrocatalysts. The main types are:

a) Intermetallic catalysts.
   Mo-Co, MoPt$_3$, MoNi$_3$, MoFe$_3$, LaCo$_5$, Ti$_{1-x}$Ni$_x$(Raney-Ni), etc.

b) Sulfides, phosphides.
   Ni-W-S, Ni-W-P, Fe-Ni-P, etc.

c) Catalysts based on Raney-Ni.
   Ni-Al-Ti, Ni-Al-Mo, Ni-Al-Cr, Ni-Zn-Ti, Ni-Zn-Mo, etc.

d) Mixed Oxides.
   TiO$_2$-RuO$_2$, TiO$_2$-IrO$_2$, Ru$_x$Ti$_{1-x}$O, RuO$_2$-IrO$_2$, etc.

e) Hypo oxide-hyper metal.
   Pt-TiO$_2$, Pt-Ru-WO$_3$, Ni-V$_2$O$_4$, etc.

The same approach as that done for the HER, ranking can be used for these materials. However, it is difficult to determine a volcano plot for the oxygen evolution reaction as textbooks$^1$ in general do not show it. The OER is a more complicated reaction than the HER; there are four electrons involved to produce one oxygen molecule as opposed to the two electrons in the HER. There are several proposed mechanisms for the OER (cf. Table 2-2) and they involve different types of intermediates interacting with the participating active site atom from the electrode.

The volcano shown in Fig. 2-3 for the HER case, with an unique intermediate being atomic hydrogen, is simple when it comes to plotting. However, there has been identified at least two intermediates for the OER, hydroxyl ion and atomic oxygen, in addition, there could be other intermediates (i.e. reactive oxygen species) not yet
been properly identified\textsuperscript{6b, 23}. It is difficult to make a plot for the OER under these circumstances.

Nevertheless, recent publications\textsuperscript{7} show a single descriptor which groups the binding energies of all the oxygen intermediates into a single value (i.e. $\Delta E_O$ (eV)). This makes possible to create a volcano plot for the OER. Fig. 2-4 shows the theoretical catalytic activity versus the single descriptor (i.e. pseudo-oxygen binding strength).

Fig. 2-4 illustrates how metal oxides have different overpotentials for the OER. The area labeled ‘electrolytic cell’ is the one of interest here, fuel cells have also been included to show how these two methodologies are related even though they operate in different directions of the water electrolysis reaction. It can be seen that for both labeled areas, their respective triangles are like mirror images around the O\textsubscript{2} equilibrium line. Therefore, a catalyst that is good for fuel cells is likely to be good for electrolytic cells, as well.

From Fig. 2-4 it can be seen that a material can be a catalyst for both oxidation and reduction. For example, transition metal doping of MnO\textsubscript{2} catalysts has been found to improve their catalytic activity for oxygen reduction\textsuperscript{14}. It can be seen in Fig. 2-4 that the triangular areas for metal and metal oxides for electrolytic cells do not completely intersect: the area for the metal oxide is shifted towards an intermediate bond strength. This is the bond strength where the catalyst is more efficient. As a consequence, metal oxides have a lower overpotential than metals for the OER.
In Fig. 2-4, RuO$_2$ is at the top of the volcano plot, very close to the 1.23 V thermodynamic minimum threshold limit for the OER; RuO$_2$ has the lowest reported overpotential for the OER in acid. Ruthenium, nevertheless, is a precious metal and its commercial use is, hence, limited. Many metal oxides have been found to have water oxidation catalytic activity$^{22a, 22b}$. There have been related studies$^{17}$ of metal oxides and hydroxides of Ni, Co, Fe, In, Sn, V and Mn. Oxides are easier to obtain than molecular catalysts, especially those from relatively abundant transition metals (cobalt and manganese) and this is important in replacing the commonly used but rather expensive platinum group metals for catalysis.

These materials could be further improved by enhancing their geometrical factor, however in practice this is cumbersome. For instance, using carbon blacks (e.g. Vulcan XC-72)$^{22a, 22b}$ as catalyst support do improve the activity. Unfortunately, at high current densities, (200-300 mA cm$^{-2}$ as used in commercial chlor-alkali electrolysis by diaphragm cells$^{28}$) such material clogs, translating into a substantial drop in the effective area due to gas bubbles not being removed properly.

Platinum group oxides for OER catalysts are expensive. In this respect, one could focus on improving the catalytic activity of running up materials. A running up material has a lower catalytic power than any of the platinum group based electrodes but could be abundant thus cheap. For example, manganese dioxide which is an important choice for the development of selective oxygen evolution electrodes, requires manganese as the raw material. There are several materials which have been studied for electrochemical water oxidation as previously mentioned. Material cost is
the most important characteristic to take into consideration, in addition, durability and overpotential are also other important variables.

Manganese is abundant, cheap and environmentally friendly. If its catalytic activity could be substantially increased then it would be a better option than platinum group based electrodes. However, MnO$_2$-based electrodes are not as good as their RuO$_2$-based counterparts. Novel techniques for synthesis for preparation of MnO$_2$ with various crystal structures, morphologies, and architectures might make these electrodes as good as RuO$_2$ electrodes. It is believed that the geometric factor as well as the electrical resistance of this material could be further improved by transition metal doping. This material concept would be identified as a ‘metal oxide based intermetallic electrode’.

Fig. 2-4 Theoretical Volcano Plot for the OER of Metals and Metal Oxides$^{7b}$.
Another supporting fact about manganese is that green plans have included on their oxygen evolving complex (OEC) of the photosystem II (PSII) a tetra manganese and calcium cluster and it is basically a calcium-manganese oxide\textsuperscript{29}. Why to talk about photosynthesis?, water electrolysis can be seen as artificial photosynthesis, it is safe to assume that information from it can be beneficial for the development of catalysts.

2.4 Catalyst Preparation

The catalyst preparation can be seen as surface engineering\textsuperscript{30}. In surface engineering there are two main processes to obtain the surface with the expected properties, and they are called the cleaning and finishing processes. Once the substrate has been selected then it has to be cleaned so that it can be finished. These processes are explained in the ASM Handbook\textsuperscript{30}, the selection of the specific type of cleaning or finishing technique is mostly based on cost. There is also a final process which is the heat treatment\textsuperscript{31}, it is not considered to be a surface engineering technique because it is a process which affects the bulk and the surface of the material. However, heat treatment is part of the catalyst preparation steps.

The techniques suitable for in this investigation are; degreasing, abrasive cleaning, electrolytic cleaning, acid cleaning and ultrasonic cleaning. These processes are selected based on relevant published articles\textsuperscript{4a, 18b, 32}, other sources\textsuperscript{30} and what is available in the laboratory. The cleaning process is not critical, the substrates to be used are normally already cleaned, however they should be cleaned to ensure that they are ready for finishing.
The main purpose of the cleaning process is to increase the adherence of the electrochemically deposited coating. In this respect, abrasive cleaning produces a mechanical lock for coating adhesion\textsuperscript{30}, making it the most important cleaning step. After cleaning, the next step is finishing.

A material can be finished by different techniques\textsuperscript{30, 33}. Between the methods for preparation of thin-film catalysts, it can be found; electrolytic deposition, spin or dip coating, high energy ball milling of powder, sol-gel, flame- and plasma- spraying of thermal decomposition with subsequent reduction to metal alloys or sputtering, arc ion plating, cold-rolling and sintering\textsuperscript{22a, 23, 33-34}. The selection of a technique is based on what it is available at the laboratory. Electrodeposition appears to be suitable as the main technique for the development of the catalyst, and this technique has both advantages and disadvantages.

A simple finishing method is electrodeposition, however, this technique\textsuperscript{33} is unsuited for producing controlled porous structures. This shortcoming could be fixed by using porous catalyst carriers or using specialized techniques like pulse electrodeposition\textsuperscript{17}, low current density electrodeposition\textsuperscript{35} and using organic additives to modify crystal growth during electrodeposition\textsuperscript{1}.

\textbf{2.4.1 Electrodeposition}

Of all of the finishing methods\textsuperscript{30}, electrodeposition is one of the simplest and most inexpensive ones. Common laboratory glassware and reagents are most of the materials needed to make an electrodeposition cell. However, this technique has limitations, such as making porous surfaces and adding new elements to a bath can
yield the formation of precipitates or other complications. For example, extreme brittleness (i.e. one of the reasons for poor adherence of a coating) can result from the presence of codeposited hydrated Fe\(^{3+}\) or Fe\(^{2+}\) oxide during iron codeposition\(^{30}\).

There has been several published works which have used this technique for the development of catalysts for electrolytic hydrogen generation. The coatings for the anode and cathode are different, and recommended cathode materials for the HER are pure or mixed metallic elements. On the other hand, recommended anode materials for the OER are pure or mixed metallic oxides. Finally, heat treatment\(^{31}\) is done after electrodeposition to improve the coating adherence, dry the surface from crystalline water, remove stress.

2.4.1.1 Electrodeposited Raney Coatings

Based on the volcano plot for the HER (Fig. 2-3), and other published works\(^{22a}\), nickel and cobalt based electrode materials for the HER, are reasonable options for further studies. The strategic approach for these materials could be improving the roughness factor of these elements.

- **Raney Nickel**

  Raney nickels have been in the field for quite some time, in 1963 and 1964, Trambouze and co-workers\(^{36}\) studied the properties of Raney nickel catalyst, which are used for heterogeneously catalyzed hydrogenation or organic substrates\(^{37}\). Raney–Ni alloy (alloy of Ni with a metal that is easily leachable in alkaline solution, as, e.g. Al or Zn) catalysts with surface area 1,000–5,000 times than that from pure Ni are referred to form\(^{4th}\) after a complete leaching. For nickel alloys a common
value of surface area is 100, however 1000 is preferred\textsuperscript{38}. It should be noted that the geometric factor is important, alloying enhances the electronic factor by sacrificing some of the geometric factor as previously described.

Raney nickel is deposited on a substrate by intrusion during nickel electrodeposition\textsuperscript{23}. The nickel solution for electrodeposition described by Watts in 1916 has been widely used as the basis for decorative nickel plating processes, as well as, engineering applications and electroforming\textsuperscript{30} (reaction shown in Eq. 2-21). Detailed description of the variables for nickel electrodeposition are found in books\textsuperscript{30}, patents\textsuperscript{39}, articles\textsuperscript{23, 34c}, etc. The nickel deposition from Watts bath is used as a binder and this is the starting point for bath plating mix and with a systematic combination of other variables, methods or reagents the active layer is prepared.

A valid approach in making an electrolytic solution for film preparation is to select one which is well documented. In this respect, a Watts bath for nickel electrodeposition is a good choice. Modifying a Watts bath is better than starting from scratch when designing an electrolytic solution. Normally, when such solutions are modified, their range of use can in essence be the same as that from the unmodified solution. For example, the current density range\textsuperscript{40} for a Watts bath is 30-110 mA cm\textsuperscript{-2}. It is expected that after a modification, this range would remain the same or be narrower.

The nickel electrodeposition is described by the following electrochemical reaction:
An initial modification to the Watts bath is when the NiCl$_2$·6H$_2$O reagent is substituted by NaCl as described by Dennis$^{41}$. This reduces the cost of the Watts bath and still yields a satisfactory nickel electrodeposition. In addition, Oda$^{39}$ gives preference to solutions containing no less than 30 g Cl$^{-1}$, under the explanation that it clears the passive layer formed on Raney nickel particles and thus reduces the oxygen content on the Raney nickel particles. These two publications$^{39, 41}$ support the idea of giving preference to high chlorine ion concentration in the Watts bath or to substitute NiCl$_2$·6H$_2$O as NaCl has a higher concentration of chlorine ion.

One documented example about the limitations for electrodeposition is found when modifying the plating bath. Hashimoto$^{42}$ and coworkers have published articles which show modified standard electrolytic solutions (e.g. Watts bath, EMD bath) but it is not explained how they fixed these limitations, when it comes to carbon and iron codeposition. Few publications have reported carbon deposition by electrolysis, lysine (i.e. the carbon source) does not completely dissolve in the modified Watts bath. In addition, iron hydroxides$^{43}$ are produced during iron electrodeposition and this is inconvenient as it makes the film brittle.

Additives to the plating solution are normally used to avoid pitting during nickel electrodeposition, however, this is solved by rotating the electrode at regular periods of time so that the attached bubbles on the surface are removed$^{23}$ or stirring the plating solution or mechanically remove them by a stirring rod. Gas evolution in

\[ \text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}^0 \]
parallel to the nickel deposition occurs, because the nickel plating is not 100% faradic efficient\textsuperscript{30}, losses are due to water electrolysis (i.e. source of bubbles) at the plating surface.

Finally, Raney nickel deposition by Watts bath is well documented as it produces well adhered films. Raney nickel particles are available at Sigma Aldrich in the form of 59/41, 79/21, 50/50, 94.3/5.7 and 98.5/1.5 combinations of nickel and aluminum and are then activated by leaching out the aluminum, this process increases the geometric factor substantially (50/50 has been considered for this research). It should be noted that Raney particles are acquired inactive, as this material is pyrophoric. The adherence of the film to the substrate can be further improved by annealing (i.e. heat treating), this is discussed as follows.

Heat treating is also described, however this technique does not improve the geometric or electronic factors of the electrodes. Heating improves the adherence of the catalyst layer to the substrate therefore its service life. In this respect, heat treating is not an objective of this research as it does not improve the catalytic properties of these materials towards the HER and OER reactions.

Depending on the purpose, heat treatment can have different conditions of ranges of temperature and time. In this respect, heat treatment carried out for this work has two purposes, drying the electrodeposited coating and partial diffusion of the coating into the substrate to increase the adherence thus a longer service life. The main objective of this research is making the electrodes energy efficient and inexpensive.
Despite of heat treating not being an objective of this research, it should be noted that it is not straight forward to adjust. For nickel based electrodes the heat-treating method is called stress equalizing\(^{40, 44}\) and the temperature range is 260 to 480 °C. The principle is not to alter the crystalline structure of the material but to diffuse nickel to the substrate to increase its service life. The heat treatment must be done in an inert environment (i.e. oxygen free) such as nitrogen, argon. Heat treating normally is seen as a variable that has a pre-establish condition and this condition is applied to any other situation. For example, a 260 to 480 °C temperature range can have a strong impact on the electrochemical properties of a nickel based electrode if the right temperature is not determined systematically.

Therefore, important attention should be taken during heat treating as macrostructures such as pore size and shape can be significantly altered thus negatively changing the properties of a material. For instance, the shape of a pore can influence the speed of removal of the evolved gas. Lasia\(^{45}\) showed mathematical models for arbitrary shaped pores related to energy efficiency of the electrode. Raush\(^{44}\) developed a mathematical model to explain overpotentials based on pores with cylindrical shape for Raney Ni. These are a few examples which show that heat treating of electrodes is not a simple task to do, in theory the structure of the material should not be changed, only enough diffusion of the active material to the substrate is sufficient.

In some cases, the crystal structure must not be altered and if the heat treatment is done incorrectly, then basically the material will change as for instance \(\gamma\)-MnO\(_2\) converted into another phase during heat treatment. For the case of nickel based
electrodes, the crystalline structure is not that important and a wider range of temperatures can be considered, however, it is recommended to be stress relieved.

- **Raney Cobalt**

  Raney cobalt has been compared to Raney nickel in terms of catalytic power for some reactions\(^{37}\). There are little publications about Raney cobalt for the HER and testing such an application with this material would be of significant interest. Raney cobalt deposition has a lot of variables in common to that from nickel deposition. Zinc-cobalt and nickel-cobalt plating are well documented\(^{30}\), in addition to pure cobalt plating\(^{46}\). Raney cobalt particles are available at Sigma Aldrich in the form of 79/21, 90/10, 99.5/0.5, 99.9/0.1 and 99/1 combinations of cobalt and aluminum and are activated by leaching out the aluminum, this process increases the geometric factor substantially (i.e. 79/21 is the selected combination for this research). It should be noted that Raney particles are acquired inactive, as this material is pyrophoric.

**2.4.1.2 Electrodeposited Manganese Dioxide Based Coatings**

Different oxides have been tested for the OER as indicated in Table 2-3. Manganese dioxides show poor catalytic power as they have substantially higher overpotentials than that of platinum group oxides. However, manganese is an abundant element and less costly than any of the platinum group metals. Most publications about manganese dioxide for relevant electrochemical purposes have been found for the development of selective oxygen evolution electrodes in seawater\(^{18b, 18e, 18f, 18h, 32, 47}\).
Manganese dioxide powders have been prepared by chemical techniques such as sol gel, thermal decomposition, and hydrothermal, however anodic and cathodic electrodeposition of MnO$_2$ are the preferred routes for synthesizing these electrodes\textsuperscript{17}. Manganese dioxide can be anodically deposited with or without buffers and surfactants and this is the method selected for this project. Manganese ions hydrolyze under anodic potentials to deposit MnO$_2$ as shown in the following equation\textsuperscript{17}:

$$\text{Mn}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2 + 4\text{H}^+ + 2\text{e}^-$$  \hspace{1cm} \text{2-22}$$

The morphology, electronic conductivity, exposed specific area, crystal structure, and defect chemistry (cation distribution and oxidation states) are modified by varying the deposition parameters and/or heat treatment\textsuperscript{17}. It is difficult to accurately
forecast the influence that a modification to the electrolytic solution can make to the electrodeposited film. One analogy to this situation would be during the invention of the light bulb, Thomas Edison tested about hundreds of compounds to develop a practical filament for the light bulb.

Manganese dioxide applications were found during chlor-alkali seawater electrolysis, it was found that the production of Cl$_2$ was lowered and the O$_2$ increased when the anode fouled due to manganese electrodeposition from seawater. It was discovered that MnO$_2$ has some selectiveness towards water oxidation.

In this respect, this discovery opened a new line of research, for example, an application was patented in 1979 by Bennett$^{47b}$, it claims that the chlorine evolution essentially ceases during electrolysis with the formation of sufficient δ-MnO$_2$. This patent shows lack of details but other works from Bennett’s$^{18h}$ show results made at 150 mA cm$^{-2}$ with a 99%+ of efficiency with no significant production of chlorine from seawater. However the polarization curves are not shown in that same publication, this is an important piece of information to be missed, not to mention stability and durability. In addition, Hiroi et al.$^{48}$, prepared manganese dioxide by Bennett’s method$^{49}$ and could not get 99% efficiency for oxygen evolution but 90% at the most.

Nearly 30 years of development, efforts in improving overpotential, stability, durability and cost have reached an acceptable level. Mainly the substrate is titanium, followed by an iridium dioxide IrO$_2$ layer and finally the active layer mainly made of manganese dioxide MnO$_2$. It has to be mentioned that further works
from that of Bennett’s have included additives to the active layer such as molybdenum\textsuperscript{18f}, iron\textsuperscript{18e}, tungsten\textsuperscript{47a} and tin\textsuperscript{47a}. Note that all these metals can be divalent element, which has the valence of two (i.e. 2), this means that other divalent transition metals could be experimented with.

There are four types of MnO\textsubscript{2} crystals mentioned for the OER; alpha (\(\alpha\)), beta (\(\beta\)), and gamma (\(\gamma\)), it should be noted that \(\beta\) and \(\gamma\) are tetravalent and \(\alpha\) is trivalent. Delta (\(\delta\)) is also reported but it gave unsatisfactory results\textsuperscript{47b}. The \(\gamma\)-MnO\textsubscript{2} also called orthorhombic nanocrystalline is the one investigated by several independent researchers\textsuperscript{18b, 18e, 18f, 32, 47a, 50} as the most appropriate for selective OER (SOER), since \(\alpha\) and \(\beta\) are unstable due to low adherence and efficiency (i.e. 70\%). For example, during electrolysis \(\alpha\)-MnO\textsubscript{2} changes the colour of the solution to red, due to manganese ions from the catalysts dissolving toward the bulk of the electrolyte. Different crystal structures are obtained by modifying the conditions of the electrolysis, for example \(\gamma\)-MnO\textsubscript{2} is electrodeposited at 90 \(^{\circ}\)C\textsuperscript{51}.

When developing an electrode material, such as one based on MnO\textsubscript{2}, one should consider the following constrains; insolubility, resistance to the mechanical and chemical effects of oxygen liberated on its surface, low oxygen overvoltage, and resistance to breakage and handling\textsuperscript{47b}. Table 2-4 shows the resistivity of some selected oxides. It can be seen that manganese dioxide is classified as a semiconductor, this property is undesirable for an electrode as energy is lost when the electricity goes through the MnO\textsubscript{2} coating. Modifying the plating conditions can improve the electrical conductivity of MnO\textsubscript{2}.  

45
The selected type of material for our work reported in this thesis is electrolytic manganese dioxide (EMD). The EMD plating solution is shown in Table 2-5, this solution has been originally developed for $\gamma$-MnO$_2$ powder. Therefore, the EMD coating is brittle, which is undesirable. In this respect, alternatives for flexible $\gamma$-MnO$_2$ coating are done by adjusting the electrodeposition conditions of the solution, one example is shown in Eberhard’s Patent$^{52}$. This method decreases the grain size of the EMD making it less brittle and better adhered.

### Table 2-5 EMD Electroplating Solution$^{51,53}$.

<table>
<thead>
<tr>
<th>Layer type</th>
<th>Temperature (°C)</th>
<th>Cathode Current Density (A dm$^{-2}$)</th>
<th>Heat Treating/Drying</th>
<th>Reagents (Analytical grade)</th>
<th>Concentration (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$-EMD</td>
<td>90</td>
<td>0.8-1.2</td>
<td>Two stages</td>
<td>MnSO$_4$·H$_2$O</td>
<td>33.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H$_2$SO$_4$</td>
<td>40-45</td>
</tr>
</tbody>
</table>

However, another alternative approach was selected to decrease the brittleness of the $\gamma$-EMD coating. Table 2-6 shows the modified electroplating EMD base solution. This other method is selected as MnO$_2$ is a semiconductor and the addition of other ions into the electroplating solution can have benefits for the electrical conductivity, brittleness and catalytic activity. This has been done to some extent by works related to selective OER in seawater electrodes.
Hashimoto\textsuperscript{18b, 18f} found that the addition of molybdenum to the EMD solution makes the film substantially less brittle and good adhered. Therefore, this solution as shown in Table 2-6 is used as the starting point in the development of films based on EMD. The film obtained by Mn-Mo-O solutions (or EMD-Mo) shows good flexibility and adherence. Another variation was done through tungsten, Mn-W-O, however, tungsten is not as good as molybdenum in improving the adherence of the electrodeposited coatings. The coatings from the EMD-Mo solution are flexible, good adhered, and are electrodeposited at high Faradaic efficiency.

Further modification to the EMD-Mo solution through adding other elements into the film could be difficult. Other reagents in addition to the Na\textsubscript{2}MoO\textsubscript{4}·2H\textsubscript{2}O for the EMD electrolytic solution is for the purpose of trying different combinations, which can be beneficial to the material for the OER. When adding iron to the EMD-Mo solution, iron hydroxides are formed during iron codeposition, this makes the film brittle. For the case of tin codeposition in the EMD-Mo, tin solubility decreases substantially as temperature increases.

Another variable of interest is the current density for the deposition of EMD. Hill\textsuperscript{54} describes two regions of current densities to produce $\gamma$-MnO\textsubscript{2}, being the one

<table>
<thead>
<tr>
<th>Layer type</th>
<th>Temperature ($^\circ$C)</th>
<th>Cathode Current Density (mA cm\textsuperscript{-2})</th>
<th>Heat Treating/Drying</th>
<th>Reagents (Analytical grade)</th>
<th>Concentration (g l\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$-EMD-Mo</td>
<td>90</td>
<td>8-12</td>
<td>Two stages</td>
<td>MnSO\textsubscript{4}·H\textsubscript{2}O</td>
<td>33.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Na\textsubscript{2}MoO\textsubscript{4}·2H\textsubscript{2}O</td>
<td>0.726</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H\textsubscript{2}SO\textsubscript{4}</td>
<td>40-45</td>
</tr>
</tbody>
</table>
above 9 mA cm\(^{-2}\) of interest, where $\gamma$-EMD is always produced. Hashimoto does the modified EMD electrodeposition at 60 mA cm\(^{-2}\) (6 A dm\(^{-2}\)), at that current density the EMD coating has good adherence and flexibility, however, the electrodeposition is Faradaic inefficient as mentioned by other works. From an engineering point of view, Hashimoto’s preferred current density for EMD deposition is flawed. The current density should be within the recommended values from literature\(^{49,52}\), where little oxygen evolution should be observed.

This is an engineering conflict from Hashimoto, if such a technology is for mass scale, inefficiencies are undesirable. In addition, gas evolution during electrodeposition changes the pH of the solution, this makes the electrodeposition process not to reach a steady state. It could be difficult to make duplicate films under such conditions.

In this respect, to control the pH, Hashimoto uses a membrane to separate the cathodic and anodic cells. It is believed that despite of the efforts to address this problem when working under the Faradaic inefficient range, the concept is fundamentally inaccurate. It is easier to adjust standard solutions to make changes in the film, however electrodeposition has limitations which cannot be fixed in some cases.

Tests such as thermogravimetric analysis should be carried out before, to identify the right conditions for heat treating. Hashimoto does not mention in his publications, how the heat treating conditions are determined. For example, in the development of Mn-Mo-Sn oxide anodes for oxygen evolution in seawater,
Hashimoto mentions that the anode panels are annealed after the active layer deposition at 650 °C for 7 hours\textsuperscript{55}. As a rule of thumb, alloys have a narrower temperature range for heat treating than that of the pure material.

EMD films are two step heat treated, the first step at 100 °C and the second step at 450-500 °C according to Hill\textsuperscript{54}. Christian in his patent\textsuperscript{56} heat-treats EMDs in two steps, the first step between 100-250 °C to drive off surface and non-crystalline water. The second step between 250-350 °C to remove lattice water. Christian\textsuperscript{56} mentions that it is an undesirable consequence of heat treating the conversion of $\gamma$-EMD to ($\gamma/\beta$)-EMD structure at temperatures $>350$ °C. ($\gamma/\beta$)-EMD is less electrochemically active\textsuperscript{56}. EMDs can be heat-treated in air, however EMD codeposited derived electrodes should be treated in an inert environment as the structure is different from that of an EMD and could be altered by oxygen available from the air at high temperature due to the heat-treatment.

Basically, the heat treatment for EMDs is to dry it from water to increase its lithium uptake capacity in lithium cells. For the OER, drying the surface from water has little importance as aqueous medium is the solution where the EMD based electrode becomes the working electrode. However, EMDs in theory could diffuse to the substrate during the heat-treatment so that its adherence increases thus its service life. For EMDs, if heat treatment is done, it must not change its crystalline structure as the electrochemical properties could be negatively altered. Structural water in EMDs can be substantially removed at 100 °C according to Ruetschi\textsuperscript{57}.
Structural water influences the electronic conductivity of EMDs as shown by Ruetschi\textsuperscript{57}.

2.5 Catalyst Testing and Characterization

The catalyst also called the active layer or coating is tested to evaluate its electrochemical and surface properties. These properties determine how energy efficient a catalyst is, and other properties such as surface area and elemental composition.

2.5.1 Electrochemical Techniques

These are the most important techniques for this research. Information about the reaction mechanism and overpotential is determined by linear voltammetry (LV) and electrochemical impedance spectroscopy (EIS).

Electrochemical reactions can be studied under different conditions. The first step for an electrochemical characterization of catalysts is defining the conditions of the test, such as temperature, pressure, electrolyte concentration and current density range. In the introduction, it is discussed that the use of nuclear energy is controversial, this discards the possibility of high temperature electrolysis (i.e. T $>$ 500 $^\circ$C)\textsuperscript{58}. The selection of low temperature or intermediate temperature electrolysis depends whether there are systems already in place where thermal energy is available and wasted. This available thermal energy can be used for electrolysis to make the reaction to occur at efficiencies higher than 100%, if the energy balance considers only the electrical energy input.
It should be noted that efficiencies higher than 100% are obtained considering the system from an engineering point of view, if a thermodynamic analysis is done then the thermal and the electrical energies are considered for the energy balance and for this case, the efficiency is always less than 100% as irreversibilities or energy losses do happen in real systems (i.e. as opposed to an ideal analysis). In our work, only low temperature electrolysis is examined (i.e. T <100 °C) due to limitations of time and budget. Intermediate temperature electrolysis (i.e. 100 °C< T <500 °C) requires the design of systems that are not available in our facilities as does high pressure electrolysis (i.e. P > 1 atm).

The next variable to be determined is the electrolyte concentration (i.e. [H⁺] and [OH⁻]). This variable is important in the sense that reduces the ohmic potential drop (IR\text{drop}) of the solution, the more ions present in the electrolyte the more electric conductive it is, in addition to a higher effective concentration or activity. The activity determines the half-cell equilibrium potential, which is the minimum potential for the reaction to happen, however, the overall equilibrium potential remains constant when both electrolytes have the same ion activity. The equilibrium potential for water electrolysis is constant at any pH as described by the Nernst equation, this value is \( E^\circ = 1.229 \text{V} \). Why is it important to work with high ionic strength electrolytes or high/low pHs? In order to see the exponential behavior or activated controlled reactions, the solution should have enough ions to avoid mass transport limitations\(^1\).

Operating with two different electrolytes to obtain low half-cell potentials for the HER and OER is possible, as found in acidic HER and alkaline OER. For this
particular case, the overall equilibrium potential would be lower than 1.229 V. However, in practice, the reaction still occurs at an overall potential that is close to that from either alkaline or acid electrolysis. When the electrolysis has two half-cell solutions which are different, then the concentration overpotential through the membrane (a.k.a. junction potential) is high and this makes the overall potential of the reaction to be the same as that from other types of electrolysis. This is equivalent to say that thermodynamics cannot be bypassed.

The equilibrium potential is determined by the electrolyte concentration. As a rule of thumb when the concentration of ions in the electrolyte is greater than 0.1 M, the assumption of concentration equals activity is no longer valid. A correction factor is used to adjust this difference, this factor is known as the individual activity coefficient (a.k.a. activity coefficient). The activity coefficient is tabulated in different sources, however, it is difficult to find activity coefficients that completely adjust to the electrolysis conditions found in this investigation and this is one of the limitations of the methodology. The activity coefficient depends on the concentration of the individual ion, background electrolyte, temperature and pressure. For example, \( pK_w \) changes as a function of background electrolyte\(^59\).

The electrolyte activity can be experimentally determined with the assistance of ion selective electrodes (ISEs), in this case the activity coefficients do not have to be determined. A pH probe which is an ISE, is used in the determination of hydrogen ion activity, it normally operates within the pH range of 0 to 14. In most cases they are effective only on the pH range of 1 to 13 and this is consistent with the rule of thumb about activity equals concentration up to 0.1 M solutions. For pHs below
zero, a special hydrogen electrode probe is required, in practice to make a hydrogen electrode to work efficiently is a difficult task.

An assumption has been done for the estimation of the activities for the H\(^+\) and OH\(^-\) ions. The concentrations of these ions are known and they are corrected with activity coefficients calculated by the MacInnes assumption and tabulated data from sources\(^60\). There is an example calculation for the activity coefficient in the appendix A. It should be noted that these activity coefficients can be greater than one.

The last variable to be determined is the current density range which should be on the Tafel behavior regime. On a I-E plot there could be distinguished four regimes\(^61\); infinite resistance, activation control (linear Tafel regime), mixed control and mass transport control as shown in Fig. 2-5. No reaction occurs in the infinite resistance regime because all electrochemical reactions have an equilibrium potential which is the minimum threshold for a particular reaction to occur. At the equilibrium potential the net reaction is zero, it is needed a certain overpotential to drive the reaction towards the product direction. In practice a reaction has to occur at a rate which makes it economically viable and it does not have to be where the thermodynamic efficiency is at its maximum. Line a shows a reaction which is purely activation controlled and line b, a reaction which is mass transport limited at the value I\(_L\).

It should be avoided the mixed and mass transport controlled regimes, as shown in Fig. 2-5, a substantial change in the applied voltage has a small effect in the current (i.e. reaction rate). The region of interest is where the Tafel curve is linear. Nevertheless, the reaction could in practice be operated in the mixed control regime
depending on financial factors. This investigation focuses primarily in the Tafel regime. At the mixed control regime a catalyst operates inefficiently, and this regime is beyond the scope of this investigation.

![Graph](image-url)

**Fig. 2-5 Electrochemical Reaction Regimes**

### 2.5.1.1 Linear Voltammetry (LV)

Linear voltammetry is a standard test for the determination of overpotential for water electrolysis. In addition, this test gives initial information about the reaction mechanism. Table 2-3 shows electrochemical data for some selected metal oxides and it is shown the Tafel slope (\( b \)) and overpotential (\( \eta \)), these two are the most basic characteristic of an electrocatalyst.

A net or overall reaction can be broken down into steps, also known as the reaction mechanism. Every step represents a reaction unity, that is, they cannot be split into more steps and they occur in sequence as shown in Eqs. 2-23 to 2-28. If the preceding step is faster or requires less energy of activation than the next one then a net accumulation of product from the preceding step will occur. This accumulation of product can be seen as a waiting queue and the overpotential of a reaction is
proportional to the size of that waiting queue\(^1\). Either excess or deficiency of electrons at the electrode due to the waiting line, makes the working potential farther away from the equilibrium potential of the overall reaction. The reaction mechanisms of interest for this research HER / OER are described in detail in the section 2.2.

A simple analogy is the waiting queues at the airport. There are several queues before getting on board of an airplane, these queues are the check-in, clearing security and getting onboard. Depending on the airline and airport there will be a net accumulation of passengers at a particular substation. Updating the systems with self check-in, better luggage x-rays, metal detector devices and organized boarding do improve the overall boarding process. Understanding which substation has the largest queue, helps to reduce substantially the time of the overall process.

The reaction step with the largest accumulation of reactants is called the rate determining step (rds). This rate determining step does vary when electrodes of different surface compositions are used and it is determined by the Tafel slope. Two different electrodes can have the same rds but different overpotentials. This situation is explained with the activation energy of the material itself. The type of interaction between the electrode and the reactant affects the energy profile of the activated specie and thus its activation energy.

Explaining how the energy profile (i.e. closely related to overpotential) of the active species is affected by the material composition is beyond the scope of this research, however, theoretical techniques such as density functional theory (DFT)
helps to identify the main variables which determine the energy profile of these species. There are relevant publications available that have worked on this direction\textsuperscript{7}. This approach still has limitations and its use should always be reconciled with experimental findings.

There are four types of ion-electrode interactions\textsuperscript{1}, the electric field, image, dispersion, and electronic forces. The catalyst material influences the image forces, dispersion forces and electronic forces. The electrical conductivity of the catalyst will make the image force easier to occur. The dispersion forces are described as instantaneous fluctuations in the electron density clouds of continuous atoms, this force between the adsorbed ion and the catalyst active site can be explained by DFT. Finally, the electronic forces which are a measure of the compatibility between the electron orbitals of the ion and catalyst active atom can be also analyzed by DTF. The analysis of these forces is out of the scope of this current study, however, a good catalyst would have a favorable combination of image, dispersion and electronic forces.

The next variable to discuss is the Tafel slope. Tafel slopes can be theoretically determined with a Butler-Volmer approach, for this a generic multistep reaction is analyzed.

\begin{align*}
A + e^- & \rightarrow B \text{ [step 1]} \quad 2-23 \\
B + e^- & \rightarrow C \text{ [step 2]} \quad 2-24 \\
\text{... further steps} \\
P + e^- & \rightarrow R \text{ [step } \bar{\gamma} \text{]} \quad 2-25
\end{align*}
\[ \nu(R + e^- \rightarrow S) \text{ [rds repeat } \nu \text{ times]} \quad 2-26 \]
\[ S + e^- \rightarrow T \text{ [step } n - \bar{\nu} - r\nu = \bar{\nu}] \quad 2-27 \]

...further steps

\[ Y + e^- \rightarrow Z \text{ [step } n] \quad 2-28 \]

where:

- \( n \): number of electrons transferred on the overall half-cell reaction.
- \( \bar{\nu} \): Electrons transferred preceding the rds.
- \( \bar{\nu} \): Electrons transferred postceeding the rds.
- \( r \): rds type of reaction (chemical=0, charge transfer=1).
- \( \nu \): Stoichiometric number.
- \( \alpha \): Forward transfer coefficient.

The Tafel slope or transfer coefficient determines the electrical energy input \((F\eta)\) to make a change in the reaction rate, and this variable is used to rank the electrode efficiency. Table 2-7 shows the estimated Tafel slope for HER with different rds. It can be seen that when the Tafel step is the rds, the Tafel slope is minimum. The Tafel path is also known as the catalytic path for this reason. When the rds is a chemical step (e.g. Tafel step) the electrode is considered to be a true catalyst.

Table 2-7 Forward Transfer Coefficients (cathodic) \(\alpha\) for Several HER rds

(Assuming \(\beta = 0.5\)) Where \(\bar{\nu}, \bar{\nu}, r, \nu\) and \(n\) are Known.

<table>
<thead>
<tr>
<th>Rate determining step (rds)</th>
<th>Electrons transferred preceding the rds ((\bar{\nu}))</th>
<th>Electrons transferred postceeding the rds ((\bar{\nu}))</th>
<th>rds reaction type ((r))</th>
<th>Stoichiometric number ((\nu))</th>
<th>Number of electrons transferred ((n))</th>
<th>Cathodic transfer coefficient ((\alpha))</th>
<th>Estimated Tafel slope mV/dec ((-d\eta/d\log{i}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volmer</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>0.5</td>
<td>118.0</td>
</tr>
<tr>
<td>Tafel</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>2.0</td>
<td>29.5</td>
</tr>
<tr>
<td>Heyrovsky</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>1.5</td>
<td>39.3</td>
</tr>
</tbody>
</table>
An anodic transfer coefficients table can be developed for the OER under the Yeager’s path. It has been published\textsuperscript{63} that Yeager’s path occurs on Platinum\textsuperscript{64}, MnO\textsubscript{x}\textsuperscript{63}, Cobalt-based and Ni-based electrodes\textsuperscript{65}. Table 2-8 shows the different Tafel slopes as a function of the rds for manganese dioxides. It can be seen that similar to the HER case, if the rds is a chemical step then the Tafel slope is minimum as seen when the third Yeager’s step is the rds. This is a proposed explanation for the identification of the rds on electrodes, however, these results come from the Butler-Volmer model which is a model with limitations.

Table 2-8 Forward Transfer Coefficients (anodic) $\bar{\alpha}$ for the OER with Yeager’s Path

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
Rate determining step (rds) & Electrons transferred preceding the rds ($\tilde{\gamma}$) & Electrons transferred postceeding the rds ($\tilde{\gamma}$) & rds reaction type ($r$) & Stoichiometric number ($\nu$) & Number of electrons transferred ($n$) & Anodic transfer coefficient ($\bar{\alpha}$) & Estimated Tafel slope mV/dec (d$\eta$/dlogI) \\
\hline
First & 0 & 2 & 1 & 2 & 4 & 0.5 & 118.0 \\
Second & 2 & 0 & 1 & 2 & 4 & 1.5 & 39.3 \\
Third & 4 & 0 & 0 & 1 & 4 & 4.0 & 14.8 \\
\hline
\end{tabular}
\end{table}

Another approach for determining the Tafel slope more precisely, adds a correction factor to the Butler-Volmer approach. The Butler-Volmer approach assumes an empty electrode surface (i.e. not blocked by any specie, intermediate radical or products)\textsuperscript{1}. By adding the surface-coverage factor ($\theta$) a correction is done as for example by the use of the Langmuir isotherm, which is the most simple isotherm of all the available ones (refer to Appendix B). Both Butler-Volmer and surface-coverage factor approaches are equivalent for describing the Tafel slope, the main difference is in the applicability, the latter approach consists in knowing the equilibrium constants for each step in the forward and reverse direction and they could be determined by electrochemical studies such as impedance spectroscopy,
and this is out of the scope of this investigation and it is only mentioned here as an alternate approach in determining the mechanism for the OER.

The Butler-Volmer model is good enough in describing the Tafel slope for the HER and OER as an initial analysis. It should be noted that the Butler-Volmer approach is useful only for the activation control regime where mass transport control is negligible. Selecting isotherms increase the complexity of the analysis. Which equation of state (i.e. isotherm) should be used for data fitting?. It could be said that the fractional coverage plays a significant role in this respect. For $\theta \rightarrow 0$ or $\theta \rightarrow 1$, the Frumkin and Temkin isotherms coincide in effect with that of Langmuir. For the intermediate range, $0.2 < \theta < 0.8$, for example, the appropriate isotherm could be a less idealistic model. For the HER on platinum under the conditions of this research, it has been found out that Frumkin-Temkin gives a good data fitting for the Tafel slope. This is one of the main reasons which make data reconciliation difficult to do, there are several isotherms models available (refer to appendix B), and in addition, adsorbed species have to be added to these models and there are still some adsorbed species being proposed.

The Frumkin-Temkin isotherm is a further modification of the simple Langmuir approach. These modifications try to account for surface roughness, inhomogeneity, and adsorbate-adsorbate interactions. For intermediate coverage (i.e. $0.2 < \theta < 0.8$) under Frumkin-Temkin conditions, and either Heyrovsky or Tafel as the rds, yields a Tafel slope of 60 mV dec$^{-1}$ from a mathematical analysis$^1$, these two different mechanisms fit the data (i.e. Heyrovsky or Tafel as rds). It has to be mentioned that the mathematical approach for the HER is simple, next to the OER
The Tafel slope has a theoretical value, however this value is affected substantially by the coverage factor as previously argued. Another factor which affects the Tafel slope is the size of the absorbed specie (i.e. Flory-Huggins isotherm), the number of water molecules replaced from the surface by the absorbed specie does change the Tafel slope but this effect is not as strong as that from the coverage factor. If the absorbed specie is small as atomic hydrogen, then it could be assumed that a few water molecules are replaced and this would change the Tafel slope by a small value.

It is out of the scope for this research the development of reaction mechanisms, this study is only limited to give an initial sound theoretical explanation. The main objective is the development of efficient catalysts. A simple example for the chlorine evolution is shown using the surface-coverage factor. This is a simplified case where one can see how difficult it becomes when the model for determining the Tafel slope becomes more complex. If Volmer is the rds for chlorine evolution and Volmer-Tafel is its path as shown in the equation 2-29.

\[
2M + 2Cl^- \rightarrow 2Cl \rightarrow M + 2e^- \rightarrow 2M + Cl_2 + 2e^- \quad 2-29
\]

Then, the rate for this reaction at high overpotentials is:
\[ i = F\vec{k}C_{\text{Cl}^-}(1 - \theta)e^{\frac{\beta EF}{RT}} \]  

where:

- $C$: Concentration (M).
- $\vec{k}$: equilibrium constant in the forward direction.

The adsorbed chloride ion intermediate is formed at the rds which is slower than the following step, therefore it is reasonable to assume $\theta \ll 1$, then $(1 - \theta) \approx 1$ and rewriting the equation 2-30:

\[ i = F\vec{k}C_{\text{Cl}^-}e^{\frac{\beta EF}{RT}} = i_0 e^{\frac{\beta \eta F}{RT}} \]  

Note that the symmetry factor ($\beta$) is replaced with the forward transfer coefficient ($\alpha$) because Eq. 2-31 refers to the overall reaction, not a specific single step. If the symmetry factor equals 0.5 and this is true for most electrochemical experiments, then the Tafel slope is 118.0 mV dec$^{-1}$. Identical result is obtained for the HER when Volmer is, as well, assumed to be the rds, this shows that both of these methods (i.e. Butler-Volmer and surface-coverage factor approaches) in explaining the Tafel slope are equivalent, under certain conditions. The corrected Butler-Volmer method is briefly shown as an alternate approach, it becomes very complicated to solve when there are more intermediates involved. This is one of the few reasons that it is not used for this investigation. In this respect, the original Butler-Volmer model is considered to be sufficient for the Tafel slope analysis.
Final comments about Tafel slopes come when considering non-linear $\log |i| \text{ vs } \eta$, which are not true Tafel slopes. Deviations from Tafel behavior could be due to reactions being fast at low overpotentials which become mass transport controlled at higher overpotentials. Tafel slopes are only meaningful at the charge transfer or activation control regime. Another type of deviation is found when there is a high electrolyte/electrode interface electrical resistance (e.g. passivated or unclean electrodes). There should always be a region where a linear Tafel behavior is found, as the applied potential is increased, all electrochemical reactions are first charge transfer controlled and later they become mass transfer controlled. However, reactions involving slow speed chemical steps can also be non-linear Tafel.

Once completed an initial explanation about the Tafel parameters, the next step is to mention the electrolytes which the electrodes can be used. The first step in selecting a material is to know if it corrodes under the environment where it is planned to be tested. In this respect, most articles test Raney nickel based electrodes in alkaline solutions. However, is it possible to use Raney nickel in acid solutions for the HER? Pourbaix and others\textsuperscript{67} give support to the use of nickel in acid HER, however at the rest potential, Ni corrodes in acid solutions. Pourbaix\textsuperscript{67b} thermodynamically shows that nickel based electrodes can be used as cathodes at practically any pH, however as anodes as in the case of the OER, he shows the formation of a passive layer of oxide or hydroxide. As an example, Kelly\textsuperscript{68} uses Raney nickel in alkaline solution for the OER and HER.
2.5.1.2 Electrochemical Impedance Spectroscopy (EIS)

EIS impedance\(^1\, 30\, 62\) is another conventional electrochemical technique. EIS determines the electrochemical characteristics of the solution, interface and electrode. This information helps to build models to simulate the electrochemical behavior of the reaction on the surface of the electrode. Another benefit is that information from linear voltammetry (LV) can be cross checked with that from EIS.

Lasia\(^69\) shows mathematical models for electrochemical impedance spectra. These models are complex even for the case of single adsorbed specie. The most basic model for electrochemical reactions is called a Randles circuit. Such a circuit is shown in Fig. 2-6, where a capacitor and a resistance are connected in parallel. The capacitor, labeled as \(C_{dl}\), represents all the adsorbed ions which may or not participate in the reaction and water dipoles electrostatically attracted to the working electrode (WE) surface in the double layer.

The resistance, labeled as \(R_{ct}\), represents the electrical resistance of the charge transfer for the electrochemical reaction (a.k.a. Faradaic resistance). EIS results give the bulk or average surface properties of the Randles circuit. This is explained by an analogy, in the design of heat exchangers, the inverse of the overall heat transfer coefficient is used to determine the resistance of the heat flow per unit of area. This coefficient is a composite of different types of heat transfer coefficients, there are different heat transfer coefficients to represent the one for the liquids from the cold and hot sides and another one for the metal tube of the heat exchanger.
In this respect, a bulk property is the combination of individual properties. The individual Faradaic resistance can be determined by the bulk property $R_{ct}$, if the amount of active sites is known. The variable that one should be after is the individual $R_{ct}$ as opposed to the total $R_{ct}$ which is an average variable. The individual charge transfer resistance ($R_{ct-ind}$) represents the electrical resistance of a single reaction, that is the resistance of the generation of one hydrogen molecule along the Volmer-Heyrovsky path. An experimental $R_{ct-ind}$ is important as it is a variable which can be reconciled by theoretical chemistry and compared to any other materials or results from other laboratories. $R_{ct-ind}$ can be determined as $\Omega$ mol$^{-1}$. In practice, this is not done as it is difficult to determine the quantity of active sites. To determine $R_{ct-ind}$ is required the amount of active sites on the electrode (i.e. effective area) or the time that it takes to produce one molecule of hydrogen from the reagents. It is more realistic the determination of the amount of active sites$^{69}$.

$R_{ct-ind}$ cannot be determined, however $R_{ct}$ is determined from equivalent circuits. The determined $R_{ct}$ sometimes is reported as $\Omega$ cm$^2$ or $\Omega$. It is inaccurate to consider $\Omega$ cm$^2$ as resistance per unit surface area. This concept is explained by Fig. 2-6(A), where the total resistance for a circuit in parallel is not linearly proportional to the amount of individual resistances. This is not the case for capacitances in parallel which can be added, this is the reason that $C_{dl}$ can be reported as F cm$^{-2}$ or F. If the total capacitance is determined, then dividing it by the apparent area, one can estimate it in units of F cm$^{-2}$.
The concept of $R_{ct\text{-}ind}$ can be seen from the Fig. 2-6. The expanded Randles circuit shows a case where there are three inert species on the electrode surface and three individual charge transfer reactions taking place. These chemical processes would require six active sites of the electrode. All these processes are in parallel so they are represented by the equivalent circuit in Fig. 2-6 (labeled A). The equivalent circuit has $R_{ct}$ and $R_{ct} = R_{ct\text{-}ind} / 3$ for 3 reactions, this is why $R_{ct}$ is considered to be a bulk surface property. $R_{ct\text{-}ind}$ is a thermodynamic variable not kinetic like $R_{ct}$.

$R_{ct\text{-}ind}$ can be further understood when looking at Fig. 2-7. This Fig. shows the reaction coordinate for the HER along the Volmer-Heyrovsky path. The activation energy ($\Delta G^\ddagger$) is required to make the reaction happen, this energy is proportional to $R_{ct\text{-}ind}$ and this is the principle to reconcile via computational chemistry the experimental data. Why $R_{ct\text{-}ind}$ is considered to be a thermodynamic variable?, this can be seen in Fig. 2-8. This Fig. shows a realistic situation for the HER on the surface of an electrode. An electrode at a certain potential and equilibrium reaches
steady state (although the pseudo-equilibrium term is more accurate). Under such a steady state, the electrode is covered by several chemical species as shown in Fig. 2-8. The relative proportion of each specie changes as a function of the working potential or it is kinetically governed. $R_{ct}$ estimation would include the $H_{ads}$ and $H_3O^+$ areas, by knowing this area, then one could determine $R_{ct-ind}$. So $R_{ct}$ is a kinetic parameter but $R_{ct-ind}$ is thermodynamic.

![Reaction coordinate](image)

Fig. 2-7 HER Reaction Coordinate for the Volmer-Heyrovsky Path.

(not to experimental scale).

In addition to $R_{ct}$ and $R_{ct-ind}$, Fig. 2-8 introduces the concepts of available and effective areas. The available area is all the area but that covered by $H_2$. The effective area is the one where the charge transfer reactions happen, this is the areas covered by $H_3O^+$ and $H_{ads}$. The inactive labeled area can be an area covered by $H_2$ which does not escape from the electrode thus insulating it, or an area which does not participate actively in any chemical process.
Fig. 2-8 HER Covering Species on the Working Electrode.

(coverage factors not to experimental scale)

- **Single Adsorbate Reaction Equivalent Circuit**

Fig. 2-9 shows the most popular equivalent circuits used to represent the hydrogen evolution reaction. The 1CPE circuit is a modification of the Randles circuit, a mathematical description of this model is done by Lasia\textsuperscript{69}. The 2CPE circuit has been developed\textsuperscript{70} for porous surfaces such as Raney nickels. Several publications\textsuperscript{71} have calculated $R_{ct}$ and $C_{dl}$ by the 2CPE equivalent circuit by the Eq. 2-32. Lasia\textsuperscript{70} explains that the use of these models can yield biased results as a material containing well defined pores is difficult to synthesize and real porous surfaces contain a distribution of various pores.
Fig. 2-9 Equivalent Circuits for One Adsorbate Reactions (a) Model Based on Mechanism, also Known as 1CPE; (b) Model for Porous Surfaces, Known as 2CPE; (c) 1CPE Model Modified to Account for the Impedance of an Oxide Layer.

Fig. 2-10 shows the 3CPE and modified 2CPE. The 3CPE model is similar to the 1CPE but it accounts the inductive behavior due to adsorbate species. This model also has mathematical support and it can occur for reactions of one adsorbed specie\textsuperscript{45}. A circuit is inductive when the phase (\(Z\)) is positive, this means that the voltage leads the current. This is the reason why the 3CPE model has an inductor (L). One example of inductive impedance is shown in Fig 6-2 (top right), where it is shown that at low frequencies, the phase (\(Y\)) is negative, this means a positive phase (\(Z\)).
The modified 2CPE model is also shown, this model has an additional capacitive loop to account for the impedance of oxides. The 1CPE and 2CPE models are modified based under the same reasoning, to account for the additional impedance from oxides. The described circuit models in Figs. 2-9 and 2-10 have electric elements which have a discrete meaning.

In all models, $CPE_{dl}$ is a constant phase element related to the double layer capacitance ($C_{dl}$) and $R_{ct}$ is the charge transfer resistance. $CPE_{dl}$ and $R_{ct}$ are related to chemical processes on the surface of the electrode. $C_p$ and $R_p$ are closely dependent on the kinetics of the reaction, specifically to the values of the rate constants of the mechanism steps. The $CPE_1 - R_1$ combination is related to the porosity of the electrode and found to be independent of the kinetics of the faradaic process. The $CPE_f - R_f$ combination represents the impedance of an oxide layer. Finally, $R_s$ is the solution resistance.

The average double layer capacitances are determined by Eq. 2-32 for the Randles 1CPE and 2CPE circuits, where $90^\circ(1-\phi)$ corresponds to a depression angle of the semicircle in the Nyquist plot. The parameter $T$ is related to the double layer capacitance and ($T = C_{dl}$ when $\phi = 1$). The average double layer capacitance is also referred as the double layer capacitance.

$$T = \tilde{C}_{dl} \phi (R_s^{-1} + R_{ct}^{-1})^{1-\phi}$$  \hspace{1cm} 2-32
Fig. 2-10 3CPE Equivalent Circuit Used for the HER in the Presence of an Inductive Loop, and Modified 2CPE to Account for the Impedance of an Oxide Layer.

- **Other Reaction Equivalent Circuits**

Lasia\(^6^9\) gives a general mathematical analysis for the EIS of OER. OER as opposed to the HER, has more than one intermediate which can be adsorbed on the surface of the electrode as this makes difficult to develop models to reconcile EIS experimental data of OER with theory. There are some cases where it is mentioned that some OER paths are not fully understood and thus can have several intermediates which would make the mathematical modeling challenging. It is beyond the scope of this research the reconciliation of OER EIS experimental data with theory and it will only be limited to data fitting from models available from the EIS software database. In addition, concepts derived from simple equivalent circuits are applied in explaining the differences between the OER EIS of the tested materials.
Lasia\textsuperscript{69} gives a general mathematical description for the electrochemical impedance for the case of two adsorbed species for any reaction. Hu\textsuperscript{72} says that no model is available for OER on noble metal oxides that has a mathematical support. There are several models available for EIS OER, some which are empirical and others with a better mathematical approach. OER is a more complex reaction than the HER and there is still adsorbed species being identified, there could be more than two adsorbed species and this would make these models inaccurate. The Randles CPE model has been used by Iseki\textsuperscript{73} for the OER.

The models 4CPE and 5CPE shown in Fig. 2-12 have been introduced by Lyons\textsuperscript{74} to model EIS OER for Ni, Co and Fe when they are covered by an oxide layer. Hu\textsuperscript{72} introduces the use of the models 1CPE, 2CPE and 5CPE' shown in Figs. 2-9 and 2-12, respectively for anodes during oxygen evolution. Iseki\textsuperscript{73}, who probably is one of the firsts modeling EIS, shows an ideal EIS OER equivalent circuit as a Randles circuit (Fig. 2-6(B)), he also shows an empirical model which is not shown in these discussions.

![Fig. 2-11 Equivalent Circuits Used in the Double Layer Potential Region.](image-url)
Iseki\textsuperscript{73} had an empirical approach developing an EIS OER equivalent circuit on noble metals. He shows the circuits 1DL and 3DL in Fig. 2-11 to model the double layer region. The 1DL circuit is the ideal case and the circuit 3DL being an adjustment of the 1DL circuit, where $R_{a/\omega}=a/\omega$ (a is a constant) is a resistance that varies with frequency. The DLs models with the 4DL (introduced by Alves\textsuperscript{75}) are for the double layer region which happens just before the OER region. The 4DL is an update of the 3DL model and these models are shown to illustrate how they are being improved. Note that, the double layer region is not of interest for this research. The Nyquist plot for a 1DL circuit would be a straight vertical line, in this respect a constant phase element (CPE) is used to replace an ideal capacitor as a CPE tilts the vertical line thus modeling the data satisfactorily.

![Diagram of equivalent circuits](image)

**Fig. 2-12 Equivalent Circuits Used in the Oxygen Evolution Potential Region in Addition to the 1CPE and 2CPE Equivalent Circuits.**
2.5.2 Microstructure, Surface and Interface Analysis

Other techniques used in the study of thin films or coatings are grouped as surface and interface analysis. These are x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM) and field emission scanning electron microscope (FE-SEM). These techniques are of worldwide use\(^{30}\) and some of them are considered to be ‘classical’.

The full potential of surface analysis is enhanced by using techniques which can support others. For example, electrochemical impedance spectroscopy gives information about surface area or roughness factor that would assist SEM analysis. Another example, oxygen content is a key variable for most coatings as it is directly proportional to electric resistance. FE-SEM or SEM equipped with chemical analysis can determine oxygen content directly and XPS can support this result and give further information about the chemical nature of the oxygen being determined by SEM/EDS.

2.5.2.1 X-ray Diffraction (XRD)

XRD is a technique used for micro-structural characterization\(^ {30}\). This technique is conventionally used for the determination of grain size and preferred orientation. It can also give information about internal stresses in the lattice. In a typical x-ray diffraction experiment, a monochromatic beam of x-rays hits the coated surface from which it is diffracted. The diffraction angles have intensities greater than zero when the Bragg’s law is satisfied at the atomic plane (hkl) in a crystal lattice.
The Bragg’s law is met when the x-ray waves hit an atomic plane which makes all the waves to become out of phase by an integer multiple of the wavelength. This makes a constructive interference between all the diffracted x-ray waves which increases its wave amplitude. The detector registers the increase in wave amplitude as an XRD peak in addition to the diffraction angle where this happens.

This technique has been used in the study of electrolytic manganese dioxide, in the determination of its crystalline structure. In the study of porous surfaces such as Raney nickel and cobalt this technique is practically not used. However, nickel and cobalt oxides negatively affect coatings in general and this technique can identified oxide peaks to support other techniques such as SEM/EDS and XPS.

2.5.2.2 X-ray Photoelectron Spectroscopy (XPS)

XPS is a technique used for the determination of the chemical state of elements. The principle of operation is based on the excitation by x-ray of a material which in turn emits electrons. Based on the total conservation of energy, the kinetic plus the binding energies of the emitted electrons equals the energy of the x-ray beam. By measuring the kinetic energy of the electrons, the binding energy (BE) is determined. The binding energy of an electron is directly related to the Coulombic attraction from the atom nucleus. This is how the chemical state of an element can be determined by measuring its binding energy values.

In practice, this technique is complicated to interpret. XPS spectra are fitted by the addition of several peaks, each one with their own fitting parameters. This technique should be used in combination with other chemical analysis techniques.
such as XRD and EDS, in addition to having an idea of the chemistry of the coating. XPS has been used in publications related to electrolytic manganese dioxide as it provides information about oxygen species in the coatings.

On the other hand, this technique has never been found to be used in the study of porous nickel and cobalt surfaces. The nature and composition of the oxygen found on a coating is of special interest as it is related to electronic properties of the coating. There are publications about the study by XPS of nickel, this information is important for the interpretation of XPS peaks related to nickel species that are formed during the electrodeposition of nickel by Watts bath.

2.5.2.3 Scanning Electron Microscope (SEM)

Scanning Electron Microscope (SEM) is a conventional technique used for the microstructural characterization of coatings and thin films. The principle of operation is based on the excitation by electrons of a material (i.e. sample) which in turn emits two types of electrons, called secondary and back scatter electrons. The secondary electrons come from atoms which have absorbed energy from the electron beam and they are directed to the detector by a positively charged Faraday cage. The information taken from the detector is used to form an image on a computer screen.

In addition, when an SEM is equipped with energy-dispersive x-ray spectroscopy (EDS) it can perform chemical analysis for $Z > 5$. EDS detects x-rays emitted by electrons from atoms of the sample. The EDS information is interpreted by the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its x-ray emission spectrum.
This technique gives information about phase distribution, grain size and shape, and surface morphology of surfaces. This technique is practically used in most publications related to porous nickel and cobalt and electrolytic manganese dioxide. SEM data interpretation is simple to do, basically the technique is an image of the surface in the order of microns.

### 2.5.2.4 Field Emission Scanning Electron Microscope (FE-SEM)

Field emission scanning electron microscope (FE-SEM) is equivalent to SEM as both give microstructural characterization of coatings and thin films. The main difference between these two techniques lies on the source of the electrons to excite the sample. FE-SEM electron beam is field emitted by an electrostatic field. In contrast, SEM electron beam is thermionically emitted by high temperature. FE-SEM gives better resolution and magnification than SEM. Similar to SEM, FE-SEM can also be equipped with energy-dispersive x-ray spectroscopy.

### 2.6 References


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3 Materials and Methods

In this section, the surface engineering methods used for the development of catalysts, are described. This includes; cleaning, finishing and characterization.

3.1 Substrate Cleaning

The working electrode (WE) assembly is shown in Fig. 3-1. The leads were made of copper and titanium for the cathode and anode, respectively, and were insulated with ferro laquer. The substrate material for these electrodes was either copper (Kocour Hull cell cathodes) or dimensionally stable anode (DSA® / iridium dioxide coated titanium panels from AMAC Corrosion anode), based on the electrode type to be produced (i.e. cathode or anode). This assembly was used as the substrate.

Fig. 3-1. Working Electrode Assembly.
In the initial step for the substrate cleaning, inspection for dirt, corrosion and other defects was done. This step was for the identification of the condition of the metal surface. Dirt was removed with a brush, if required, then the other cleaning steps were done (sections 3.1.1 and or 3.1.2).

3.1.1 Cathode Substrate Cleaning

The copper panels (Kocour Hull cell cathodes) were cleaned in this order; the first step was to remove the plastic film (if any) on the substrate. Polishing with fine emory paper, degreasing with acetone, deionized (DI) water rinsing, and ultrasonic bath cleaning for one minute. These steps were followed by alkaline electrocleaning (Table 3-1), DI water rinsing, acid pickling (Table 3-1), and drying. The last steps, including alkaline and acid cleaning, were repeated until water broke free from the surface.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Analytical grade reagents</th>
<th>Concentration</th>
<th>Time</th>
<th>Temperature (°C)</th>
<th>Other specs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline cleaner</td>
<td>(NaOH)</td>
<td>1.5 M</td>
<td>1 minute</td>
<td>Ambient</td>
<td>The work is made anodic (+) at 30 mA cm(^2)</td>
</tr>
<tr>
<td>DI Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>(HCl)</td>
<td>10% by weight</td>
<td>5 seconds</td>
<td>Ambient</td>
<td>N/A</td>
</tr>
<tr>
<td>DI Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.1.2 Anode Substrate Cleaning

The iridium dioxide panels (AMAC Corrosion) were cleaned in this order; degreasing with acetone and DI water rinsing. These steps were followed by alkaline electrocleaning (Table 3-2), DI water rinsing and drying with tissue paper, acid
pickling (Table 3-2), DI water rinsing and drying. The last steps, including alkaline and acid cleaning, were repeated until water broke free from the surface, when appropriate.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Concentration</th>
<th>Time</th>
<th>Temperature (°C)</th>
<th>Other specs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline cleaner (NaOH)</td>
<td>10 M</td>
<td>5 min</td>
<td>Ambient</td>
<td>The work is made anodic at 100 mA cm⁻²</td>
</tr>
<tr>
<td>DI Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphuric acid (H₂SO₄)</td>
<td>1 M</td>
<td>1 min</td>
<td>Ambient</td>
<td>N/A</td>
</tr>
<tr>
<td>DI Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 3.2 Surface Finishing-Electrodeposition

The electrodeposition was selected as the finishing method for the catalysts. For this, the set up shown in Fig. 3-2 was used. It should be noted that when the working electrode (WE) had one face insulated, then one of the counter electrodes was turned off. The instruments and materials used for the plating set up are described in the following list.

An acrylic inner half-cell with membrane (purpose built), Nafion (Sigma-Aldrich 292567 Nafion perfluorinated membrane) as the membrane, a 2-liter beaker as outer half-cell, magnetic stirrer, thermometer, and 316 stainless steel or nickel counter electrodes, as required. Plus a power supply, a box for electrical connections (purpose built), a hot plate and an oil bath.
3.2.1 Cathode Finishing

This section describes the procedures for the cathode layer application (Raney nickel and cobalt electrodes). Raney Ni was acquired from Merck as a 50/50 nickel-aluminium alloy powder Cat. No. 8.06749.0250 and Raney Co from Sigma-Aldrich as a 79/21 cobalt-aluminium alloy powder Cat. No. GF11684415. A nickel Watts solution was used for the electrodeposition as the binder for the Raney particles. Table 3-3 indicates the general characteristics of Watts baths.

The specific solution used for the electrolytic cathode preparation is described in the articles about Raney nickel and cobalt (Chapters 6 and 7). The counter electrode used was nickel (Kocour Hull cell anodes) and it was covered during electrodeposition with cotton bags to avoid pitting. The inner half-cell container was not used as nickel electrodeposition is highly faradic efficient\(^1\). The copper WE was
made cathodic at 30 mA cm\(^{-2}\) and had dimensions of 20 x 10 x 1 mm or 15 x 10 x 1 mm. Once the electrodeposition was completed, an initial inspection using Scotch tape to check the deposit adherence was done. Those samples which failed the ‘Scotch’ test were discarded.

### Table 3-3. Watts Nickel Electroplating Solution\(^1\).

<table>
<thead>
<tr>
<th>Layer type</th>
<th>Temperature (°C)</th>
<th>Cathodic current density (A dm(^{-2}))</th>
<th>pH</th>
<th>Reagents (Analytical grade)</th>
<th>Concentration (g l(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Watts</td>
<td>44-66</td>
<td>3-11</td>
<td>2-4.5</td>
<td>NiSO(_4)-6H(_2)O</td>
<td>225-400</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NiCl(_2)-6H(_2)O</td>
<td>30-60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H(_3)BO(_3)</td>
<td>30-45</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>No other additives</td>
</tr>
</tbody>
</table>

The panels (i.e. Raney Ni and Raney Co) were activated with full leaching by immersion in a 6.25 M NaOH solution at 70 °C for 1h\(^2\). Then panels were DI water rinsed and dried at 70 °C in air for 1 hour.

#### 3.2.2 Anode Finishing

This section describes the procedures for the anode layer application. An electrolytic manganese dioxide (EMD) solution is used for electrodeposition and Table 3-4 indicates the characteristics of the EMD base mix plating solution.

The set up used for the electrolytic anode preparation is shown in Fig. 3-2. The counter electrode used was stainless steel (SS) (Kocour Hull cell anodes) with dimensions of 100 x 75 x 1 mm. The inner half-cell container was used to suppress solution from the external half-cell getting in contact with the internal half-cell
solution. The DSA® WE was made anodic at 10 mA cm$^{-2}$ and had dimensions of 20 x 10 x 1 mm or 15 x 10 x 1 mm. An initial inspection using ‘Scotch’ tape to check the deposit adherence was done. Those samples which failed the ‘Scotch’ test were discarded. After electrodeposition the panels were DI water rinsed and dried at 100 °C in air for 1 hour.

<table>
<thead>
<tr>
<th>Layer type</th>
<th>Temperature (°C)</th>
<th>Anodic current density (A dm$^{-2}$)</th>
<th>Heat treating/drying</th>
<th>Reagents (Analytical grade)</th>
<th>Concentration (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-EMD</td>
<td>90</td>
<td>0.8-1.2</td>
<td>Two stages</td>
<td>MnSO$_4$·H$_2$O</td>
<td>33.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H$_2$SO$_4$</td>
<td>40-45</td>
</tr>
</tbody>
</table>

3.3 Electrode Characterization

The developed electrodes were characterized to determine their catalyst activity, and other surface properties. These tests included linear voltammetry (LV), electrochemical impedance spectroscopy (EIS) as the electrochemical tests. In addition, scanning electron microscopy (SEM/EDS), field emission scanning electron microscopy (FE-SEM/EDS), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) were made.

3.3.1 Electrochemical Tests (LV and EIS)

The LV and EIS tests have the same set up as shown on the Fig. 3-3. It consisted of a three electrode set up remotely controlled by a BioLogic VSP potentiostat. The reference (RE) and counter electrode (CE) were Ag|AgCl satd. KCl and glassy carbon with the dimensions of 40 x 50 x 1 mm, respectively (alternatively Platinized
Pt as CE was used, 10 x 10 x 1 mm). The samples were used as working electrodes, their dimensions were 20 x 10 x 1 mm or 15 x 10 x 1 mm.

The electrolyte solution was either 2 M H₂SO₄ or 2 M KOH at 25 °C, based on the test requirements. The solution temperature was regulated by an external water bath. The reference electrode was placed in the vicinity of the working electrode (~2 mm) with a Luggin capillary.

### 3.3.1.1 Linear Voltammetry

After following the previous procedure the experiment was set up as shown in Fig. 3-3. The BioLogic VSP potentiostat was configured as follows; the $IR_{\text{drop}}$ compensation was done by the current interruption method where the solution resistance was determined and compensated (at 80 % compensation). The current density range was set up arbitrarily within the ±(1 to 100) mA cm⁻² range and a scan rate within the recommended value⁴ of 0.1-2 mV s⁻¹.

![Fig. 3-3. LV and EIS Experimental Set up.](image-url)
The equilibrium potential was determined by adjusting the concentrations to activities with the MacInnes assumption (a full calculation example is found in appendix A). The Ag|AgCl satd. KCl potential was taken as 197 mV vs. SHE. Finally, the geometric or apparent area of the coating was used in the determination of current densities. This technique was used for the determination of overpotential curves and Tafel slopes (a full calculation example is found in appendix A).

3.3.1.2 Electrochemical Impedance Spectroscopy

After following the previous explanation and setting up the experiment as shown in Fig. 3-3. The BioLogic VSP potentiostat was configured as follows; EIS tests were done with a stabilization time (t_s) of 3 min., potential amplitude (V_a) of 5 mV, and a frequency range of 50 mHz to 20 kHz (unless otherwise specified). The samples acted as working electrodes. The WE potential (E_i and E_f) were selected depending on the test with certain degree of arbitrariness to achieve current densities within the 1 to 10 mA cm⁻² range. These variables are identified in Fig. 3-4. This technique provided impedance data for the HER and OER and was fitted with equivalent circuit models. The fitting software used was EC-Lab® from BioLogic Science Instruments. Important information obtained by this technique was the charge transfer resistance (R_{ct}) of electrochemical reactions and roughness factors (r_f).

3.3.2 Surface Tests

For these tests the samples were made by cutting the finished substrate panels from Fig. 3-1 into square sections of 5 x 5 mm in a guillotine. Then these samples
were further tested by the following described techniques with the subheadings 3.3.2.1. to 3.3.2.4.

### 3.3.2.1 X-ray Diffraction

Thin film XRD diffraction was performed by a multi-purpose thin-film X-ray diffractometer, model: RIGAKU, D/MAX-2500 with an incident wavelength of Cu Kα (λ=1.54Å), unless otherwise specified. The detector was gradually rotated to obtain X-ray diffraction patterns at a scan rate of 2° min⁻¹. The generated XRD spectra peaks from the samples were matched to those from JCPDS files. Peak position, intensity and width were analyzed and Miller indices were also determined.

![Fig. 3-4. Staircase Potentio Electrochemical Impedance Spectroscopy (SPEIS).](image)

The reference numbers for copper, nickel and cobalt phases were; Cu: 00-004-0836, Ni: 01-071-3740, Copper-Nickel: 01-080-5767, Co: 00-015-0806, NiO: 00-
In the case of MnO$_2$ phase analysis, published articles were used for peak identification.

### 3.3.2.2 X-ray Photoelectron Spectrometer

X-ray photoelectron spectroscopy (XPS) was done with a MultiLab 2000. The X-ray source of this instrument is Al K $\alpha$. The mode of operation was fixed analyzer transmission (FAT), also known as constant analyzer energy (CAE). Peak calibration was done with the carbon C(1s) peaks. Peak position, intensity and width were analyzed by comparing results from different samples with others of similar chemical composition. Peak analysis was done with the purpose of identifying changes in the composition of an element with different oxidation states or elements with the same oxidation state but belonging to different molecular structures.

### 3.3.2.3 Scanning Electron Microscope

This instrument was used as a tool to support results from the FE-SEM. Scanning electron microscopy (SEM) was done with a JSM-6000 instrument. This instrument has a magnification of 10X to 60,000X which is lower than that from FE-SEM. This instrument is also equipped with energy dispersive spectroscopy and these results were used to support those obtained by FE-SEM EDS.

### 3.3.2.4 Field Emission Scanning Electron Microscope

Micrographs were taken by field emission scanning electron microscopy (FE-SEM), model JEOL, JSM-7000F. This instrument has a resolution of 1.2 nm at 30 kV and magnification of 10X to 500,000X. It is also equipped with energy dispersive spectroscopy (EDS) with a resolution of 133 eV and it is capable of analyzing light
elements (Be4 to U92). Surface morphology of the samples was obtained by FE-SEM, and elemental analysis was done by EDS.

3.4 References


Chapter 4

4 Modified Electrolytic Manganese Dioxide (MEMD) for Oxygen Generation in Alkaline Medium

4.1 Introduction*

Global warming and fossil fuel dependence are two closely related topics that have an important negative impact on society. In contrast, green technologies emerging from a hydrogen economy have several advantages as they are environmentally friendly, renewable but still not cost-effective\(^1\). Any approach to lower the costs of these green technologies should be in the direction to make them competitive and feasible for practical applications.

Electrolytically generated hydrogen is believed to be an alternative practical approach to support hydrogen economy\(^{1a, 1b, 2}\). Improving this process, as for example, through the use of proton exchange membrane (PEM) cells, has proven to minimize the \(IR_{\text{drop}}\) thus saving energy and costs. Another approach in making this technology cost-effective is finding substitutes for conventional anode materials such as those from the costly platinum group oxides (e.g. RuO\(_2\), IrO\(_2\)). Platinum group materials are expensive thus a cheap substitute for these materials is needed. In this respect, in our work reported here, we have used inexpensive electrolytic manganese dioxide (EMD) as a starting material, most appropriate candidate for oxygen generation in alkaline medium. \textit{J. Solid State Electr.} \textbf{2015}, \textit{19} (4), 1133-1142.

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Evolution reaction (OER). If its electrochemical/catalytic activity could be substantially increased then it would be a better option than platinum group based electrodes. With this as an objective, we have incorporated a range of transition metal doping as additives to the parent electrolytic manganese dioxide (EMD) and termed as ‘modified EMD (MEMD)’. The geometric factors as well as electrical resistance of the MEMDs are found to be enhanced through doping. Dopants also act as mediators in oxygen reaction mechanism while stabilizing the MnO₂ structure.

Any material can be altered by modifying its electronic and geometric factors to make it more electroactive. As for an instance, changing the grain size, chemical composition and using porous catalyst carriers can prove to be beneficial toward the oxygen evolution reaction. Decreasing the grain size of a material increases its surface area or roughness factor, which results in enhancing geometric factor. Modifying the oxygen basicity/acidity of the coating can also influence the electrochemical activity of a material. This can be evidenced through the shift in the oxygen peak position in X-ray photoelectron spectroscopy analysis which is discussed in this chapter in the subsequent sections. This may be related to enhancement in the electronic factor of the coating.

There have been previous publications about the modification of the EMD plating solution to make this material more energy efficient and selective toward the OER in seawater. We have used a similar approach, by modifying the EMD plating solution and testing the coating for the OER in alkaline media. EMD is brittle and adding molybdenum has been found to improve its adherence, additional additives in the electrolytic bath have been reported in the range of 0 to 9 mM. In the current
work, we have used vanadium, tungsten and cobalt as an additive in a range lower than 6 mM. In addition, this work reconciles improvements found in the overpotentials of the coatings by electrochemical impedance spectroscopy (EIS). It should be noted that EMD materials reported earlier for OER studies did not include EIS techniques.

In the present chapter, modified EMD (MEMD) coating for alkaline OER have been investigated using electrochemical techniques and a fundamental understanding of these results have been made by determining the roughness factors, water content and oxygen acidity of the coatings.

4.2 Theory

The overall oxygen evolution reaction (OER) in alkaline media for a half-cell is represented as

$$4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \quad 4-1$$

This reaction has several mechanisms, Delgado\textsuperscript{1a} proposed several OER mechanisms through several notable authors such as Bockris\textsuperscript{4}, Krasil’schikov\textsuperscript{5}, Kobussen\textsuperscript{6} and O’Grady\textsuperscript{7}. There is a common initial step in all of these proposed mechanisms as shown by Eq. 4-2. The mechanism steps involve a range of different surface adsorbed intermediates such as MO, MOOH, or physisorbed peroxide species depending on the reaction mechanism followed by the anode material. However, most reaction paths show two adsorbates. In this respect, efforts in simplifying the analysis of the OER mechanism have led to a mathematical artifact. An oxygen catalytic activity descriptor shows certain correlation between catalytic
OER activity and surface bond energy of OH\(^8\). The electrochemical oxide path in alkaline solution described by Bockris\(^9\) is shown by Eqs. 4-2 to 4-4. This path predicts Tafel slopes of 120, 40 and 30 mV dec\(^{-1}\) when the rate determining step (rds) is the Eq. 4-2, 4-3 or 4-4, respectively\(^{10}\).

\[
\begin{align*}
\text{M} + \text{OH}^- & \rightarrow \text{M-OH} + e^- \quad 4-2 \\
\text{M-OH} + \text{OH}^- & \rightarrow \text{M-O} + \text{H}_2\text{O} + e^- \quad 4-3 \\
2\text{M-O} & \rightarrow 2\text{M} + \text{O}_2 \quad 4-4
\end{align*}
\]

It is not the purpose of this current chapter to propose a mechanism but the facts introduced here are to support the selection of the model used to fit the EIS data. Doyle and Lyons\(^{11}\) used a modified 1CPE for oxygen evolution and it is specified that the 1CPE models the EIS spectra for the OER in alkaline media. Hu also used a modified 1CPE for oxygen evolution but in acid media\(^{10}\). These results support the use of an equivalent electrical circuit for one adsorbate. Lasia analytically derives the electrochemical impedance for one adsorbate reactions, commonly represented by the 1CPE circuit\(^{12}\). There is also another model available for one adsorbate reaction but mainly used for porous surfaces, this model is commonly known as 2CPE\(^{13}\). Fig. 2-9 (in chapter 2) shows the most common models for one adsorbate reactions.

The double layer capacitance (\(CPE_{\text{dl}}\)) is used to determine the area of the electrode that participates in the reaction. In this respect, Eq. 2-32 (in chapter 2) determines the average double layer capacitance for one adsorbed specie reactions. Combining this information with an estimated \(C_{\text{dl}}\) of 60 \(\mu\)F cm\(^{-2}\) for a smooth metallic electrode\(^{10}\), a roughness factor is determined.
To determine the model to use from Fig. 2-9, an initial analysis of the resistance of the oxide layer \( R_f \) should be carried out. \( R_f \) can be estimated with the relation for resistors with uniform cross-section as \( \rho = R A l^{-1} \), where \( \rho \), \( R \), \( A \) and \( l \) are the electrical resistivity, electrical resistance, cross-sectional area of the electrode and the length of the coating. Typical resistivities for IrO\(_2\) is \( 6 \cdot 10^{-5} \) Ohm cm and for EMDs are found within the 0.1 to 10 Ohm cm range. These figures allow neglecting their effect on impedances when considering coating lengths in the vicinity of \( 10^{-5} \) m (10 \( \mu \)m) and a cross-sectional area of 1.5 cm\(^2\). Only TiO\(_2\) (\( 10^{13} \) Ohm cm) could affect the impedance, if it is present in reasonable amounts on the Ti electrode substrate.

4.3 Materials and Methods

4.3.1 Electrode Preparation

The plating station consisted of the electrolyte bath, a power supply, a 316 stainless steel sheet comprising 70 x 50 x 1 mm, and a IrO\(_2\)/Ti sheet comprising 10 x 15 x 1 mm (DSA\(_{®}\) Acquired from AMAC Corrosion Co.) with one face insulated by ferro-lacquer, as counter and working electrodes, respectively. An internal half-cell vessel connecting the solutions by a Nafion membrane was used. The solutions used in the preparation of modified EMDs are tabulated in Table 4-1. The samples were electrodeposited at \( i = 10 \) mA cm\(^{-2}\) for 20 minutes. The samples were dried at 100 °C in an oven for a period of 1 hour in air atmosphere as the last preparation step.

4.3.2 Linear Voltammetry (LV)

A standard three electrode set up including a BioLogic VSP potentiostat was used. The reference (RE) and counter electrode (CE) were Ag|AgCl satd. KCl and a
platinized platinum sheet with the dimensions of 10 x 10 x 1 mm, respectively. EMD based electrodes were made anodic in 2 M KOH solutions in the OER regime. The scan rate was 0.1 mV s\(^{-1}\) and the scan range was set arbitrary from low to high current densities in the range of 100 mA cm\(^{-2}\). The \(IR_{\text{drop}}\) compensation was carried out by the current interruption method. The potential of the Ag|AgCl satd. KCl electrode was taken as 197 mV vs. SHE and all the tests were done at 25 °C.

Table 4-1 Electrolytic Solutions used in the development of MEMD anodes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reagents (Analytical grade)</th>
<th>Concentration g l(^{-1})</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnMoO</td>
<td>MnSO(_4) (\cdot) 5H(_2)O</td>
<td>33.802</td>
<td>3a-c, 3e</td>
</tr>
<tr>
<td></td>
<td>Na(_2)MoO(_4) (\cdot) 2H(_2)O</td>
<td>0.726</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H(_2)SO(_4)</td>
<td>42.5</td>
<td></td>
</tr>
<tr>
<td>MnMoVO</td>
<td>V(_2)O(_5)(^*)</td>
<td>Satd. &lt; 0.546</td>
<td>--</td>
</tr>
<tr>
<td>MnMoWO</td>
<td>Na(_2)WO(_4) (\cdot) 2H(_2)O(^*)</td>
<td>Satd. &lt; 0.990</td>
<td>3e</td>
</tr>
<tr>
<td>MnMoCoO</td>
<td>CoSO(_4) (\cdot) 7H(_2)O(^*)</td>
<td>1.687</td>
<td>--</td>
</tr>
</tbody>
</table>

\(^*\) in addition to the solution of the MnMoO sample

4.3.3 Electrochemical Impedance Spectroscopy (EIS)

EIS consisted of 3 consecutive scans over the frequency range from 100 kHz to 0.02 Hz performed one after another at potentials in the OER regime. The applied ac sinusoidal voltage had amplitude of 5 mV at 25°C. This test was done in sequence after linear voltammetry.

4.3.4 Surface Characterization

The crystallinity of the deposits was studied by a Siemens X-ray diffractometer (XRD) with Philips Co-K\(\alpha\) radiation (1.7902 Å). X-ray photoelectron spectroscopy (XPS) was used to examine the surface chemistry of the deposits with a ThermoMultilab 2000. Carbon, C(1s), was used as the reference spectrum. Finally,
the morphology of the deposits was analyzed by scanning electron microscopy (SEM) equipped with energy dispersive analysis (EDS) for qualitative elemental analysis using a JEOL JSM-6000 SEM/EDS instrument. As received EMD was used as reference and labeled EMD control, this sample was used for XRD and XPS tests.

4.4 Results and Discussions

4.4.1 Tafel Plots

Matsumoto reported IrO$_2$ electrodes having Tafel slopes ($b$) ranging 40 to 50 mV dec$^{-1}$ at low overpotentials ($\eta$) and $\eta = 250$ to 280 mV at a current density $i = 10$ mA cm$^{-2}$ (note that the $i$ value is different in Table 4-2) for OER in alkaline media at low temperatures$^{14}$. In contrast, MnO$_2$ based electrodes have been reported with $b = 110$ to 197 mV dec$^{-1}$ at low overpotentials and $\eta = 470$ to 640 mV at a current density$^{14} i = 10$ mA cm$^{-2}$. Our results on modified EMDs are in agreement to those of published results, as shown in Fig. 4-1.

A dimensionally stable anode has been used to compare the performance metrics of our developed MEMDs. Table 4-2 shows the Tafel parameters of all the samples that have been used in the current work along with DSA. It can be seen that the MEMD samples shows an enhanced overpotential to that of the reported work$^{14}$ (as previously quoted). The MnMoVO sample in particular, shows a substantial overpotential improvement, it gets to the proximity of that from DSA$^\text{®}$ at $i = 100$ mA cm$^{-2}$. It is believed that the improvement in the observed overpotentials on the samples is primarily a combination of increase in the roughness factor and low water content. Another considered variable is the oxygen acidity of the coating. If oxygen from the electrode surface layer becomes an active site during the OER, then the
bond strength of the electrons of its outermost orbit could have an important influence when it comes to OER overpotential, this is referred as its acidity\textsuperscript{15}.

Fig. 4-1 Tafel Plot of the MEMD Electrodes in 2 M KOH Solution.

In addition to overpotential, another variable of interest is the Tafel slope. A Tafel slope of about 40 mV dec\textsuperscript{-1} can be theoretically reconciled by assuming Eq. 4-3 as the rds\textsuperscript{10}. This is the case for the DSA\textsuperscript{®}. However, a slope in the vicinity of 60 mV dec\textsuperscript{-1}, as in the case of MnMoCoO, is not straight forward to reconcile. There are two approaches which could yield a theoretical 60 mV dec\textsuperscript{-1} slope. The first one, by adjusting the OER mechanism by adding more steps\textsuperscript{10}, alternatively one could introduce different isotherms to account for non-idealities of the electrode surface.

4.4.2 Electrochemical Impedance Spectroscopy

As described in the theory section, the equivalent circuit selected to model the EIS data is the 1CPE model. The modified 1CPE model was not considered because SEM analysis (section 4.4.5) showed no TiO\textsubscript{2} between the DSA\textsuperscript{®} and the Ti
substrate. Poor substrate cleaning during the DSA® preparation could yield a TiO₂ layer that would add a capacitive loop to the experimental impedance. Fig. 4-2 shows the Nyquist diagrams for the electrodes under study.

Table 4-2 Experimental Tafel Parameters of the MEMD Electrodes for the OER in 2 M KOH, Ranked by η₁₀₀.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>b (mV dec⁻¹) low η</th>
<th>high η</th>
<th>η₁₀₀ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSA</td>
<td>41</td>
<td>137</td>
<td>349</td>
</tr>
<tr>
<td>MnMoVO</td>
<td>57</td>
<td>136</td>
<td>391</td>
</tr>
<tr>
<td>MnMoWO</td>
<td>45</td>
<td>173</td>
<td>422</td>
</tr>
<tr>
<td>MnMoO</td>
<td>52</td>
<td>276</td>
<td>499</td>
</tr>
<tr>
<td>MnMoCoO</td>
<td>61</td>
<td>291</td>
<td>503</td>
</tr>
</tbody>
</table>

Fig. 4-2 shows good agreement between the experimental data and the 1CPE model. The selected overpotential range for EIS analysis belongs to the region where the Tafel slope is under low overpotential. This ensures the study of a region with the same rds thus similar parameters for the 1CPE between samples were expected and found. Tables 4-3 to 4-5 show the 1CPE fitted parameters for the samples under study. Special consideration is taken for the CPEdl and Rct elements which give an indication about the active surface area and how it decreases as a function of gas evolution rate. The best way to analyze the impedance parameters is through the fitting curves. From such fits the following parameters have been obtained: Rct, CPEdl for the range of dopants as additives used in the parent EMD material.
Maximum roughness factors determined by Eq. 2-32 do not show a clear trend when considering the overpotential rank of the samples. Ranking the electrodes by roughness factors (in parentheses), MnMoWO (485), MnMoVO (425), DSA (330), MnMoO (293), MnMoCoO (198), this observed order is different from that of Table 4-2. This result partially explains the gradual overpotential decrease found in the modified EMD samples. It is believed that a complete explanation about the overpotential improvement should consider other properties of the coatings such as water content and oxygen acidity within the coating. Other results of interest are the
decrease of the $CPE_{dl}$ and $R_{ct}$ as a function of $i$, this is expected as the OER reduces
the available area for the reaction when its rate is increased. The constant phase
elements show deviations from the ideal capacitance as determined by $\alpha$ with values
about 0.7 to 0.9, these results are in agreement to those found in similar studies done
for the OER$^{11a}$.

Table 4-3 EIS Modeled Data of the DSA and MnMoVO Electrodes for Alkaline
OER with a Solution Resistance of $R_s = 0.2 \ \Omega$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\eta$ (mV)</th>
<th>$i$ (mA cm$^{-2}$)</th>
<th>$CPE_{dl}$ (F s$^{-1}$)</th>
<th>$\alpha_1$</th>
<th>$R_{ct} \times 10^{-2}$</th>
<th>$C_p$ (F s$^{-1}$)</th>
<th>$\alpha_2$</th>
<th>$R_p \times 10^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSA</td>
<td>200</td>
<td>0.24</td>
<td>2.28</td>
<td>0.937</td>
<td>2.538</td>
<td>9.05</td>
<td>0.978</td>
<td>26.34</td>
</tr>
<tr>
<td></td>
<td>225</td>
<td>0.97</td>
<td>2.25</td>
<td>0.939</td>
<td>2.676</td>
<td>8.92</td>
<td>0.929</td>
<td>9.01</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>3.91</td>
<td>2.16</td>
<td>0.948</td>
<td>3.33</td>
<td>8.63</td>
<td>0.882</td>
<td>3.081</td>
</tr>
<tr>
<td></td>
<td>275</td>
<td>15.76</td>
<td>1.80</td>
<td>0.962</td>
<td>7.00</td>
<td>9.30</td>
<td>0.837</td>
<td>1.054</td>
</tr>
<tr>
<td>MnMoVO</td>
<td>225</td>
<td>0.37</td>
<td>3.34</td>
<td>0.869</td>
<td>3.52</td>
<td>8.49</td>
<td>0.851</td>
<td>43.4</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>1.01</td>
<td>2.81</td>
<td>0.896</td>
<td>3.36</td>
<td>8.56</td>
<td>0.854</td>
<td>15.03</td>
</tr>
<tr>
<td></td>
<td>275</td>
<td>2.78</td>
<td>2.28</td>
<td>0.922</td>
<td>2.940</td>
<td>8.64</td>
<td>0.856</td>
<td>5.21</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>7.68</td>
<td>1.76</td>
<td>0.949</td>
<td>2.040</td>
<td>8.71</td>
<td>0.859</td>
<td>1.81</td>
</tr>
</tbody>
</table>

* additional significant figures due to smaller standard deviations.

In conclusion, electrochemical impedance spectroscopy data gives an insight on
the geometric factor of the prepared electrodes toward the OER. However, to get a
complete picture, changes in the electronic factor need to be assessed. In this respect,
X-ray photoelectron spectroscopy and X-ray diffraction tests are used in combination
to EIS, as they give information about the surface chemistry and structural aspects of
the deposited electrode.

4.4.3 XRD Spectra

XRD spectra of EMDs have been reported earlier$^{16}$. EMDs are described as $\gamma$-
MnO$_2$, which is a combination of ramsdellite and pyrolusite. In addition, EMDs have
$\varepsilon$-MnO$_2$ but it is often neglected due to its low phase concentration. Strong XRD
peaks for EMDs are the 021 and 110\textsuperscript{16b}. Figure 4-3 shows the XRD spectra for all the MEMD electrodes, including the EMD control electrode and the catalyst carrier (i.e. substrate). Identified peaks on the EMD control are the 021 and 002. There is also a 110\textsuperscript{*} peak indicated, however this peak is also shown by the substrate and hence removed from further analysis.

Table 4-4 EIS Modeled Data of the MnMoWO and MnMoO Electrodes for Alkaline OER with a Solution Resistance of $R_s = 0.2 \, \Omega$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\eta$ (mV)</th>
<th>$i$ (mA cm\textsuperscript{-2})</th>
<th>$CPE_{dl}$* ($F_s^{-1} \cdot \Omega^{-1}$)</th>
<th>$R_{ct}$*10\textsuperscript{-2} (\Omega)</th>
<th>$C_p$*10\textsuperscript{-2} ($F_s^{-1} \cdot \Omega^{-1}$)</th>
<th>$R_p$* ($\Omega$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnMoWO</td>
<td>250</td>
<td>0.34</td>
<td>3.66</td>
<td>0.889</td>
<td>3.44</td>
<td>9.24</td>
</tr>
<tr>
<td></td>
<td>275</td>
<td>1.22</td>
<td>3.00</td>
<td>0.911</td>
<td>2.507</td>
<td>10.35</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>4.40</td>
<td>2.33</td>
<td>0.933</td>
<td>1.827</td>
<td>11.45</td>
</tr>
<tr>
<td></td>
<td>325</td>
<td>15.92</td>
<td>1.67</td>
<td>0.955</td>
<td>1.332</td>
<td>12.55</td>
</tr>
<tr>
<td>MnMoO</td>
<td>275</td>
<td>0.54</td>
<td>2.45</td>
<td>0.838</td>
<td>3.80</td>
<td>11.03</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>1.64</td>
<td>1.82</td>
<td>0.871</td>
<td>3.55</td>
<td>10.43</td>
</tr>
<tr>
<td></td>
<td>325</td>
<td>4.94</td>
<td>1.198</td>
<td>0.903</td>
<td>2.868</td>
<td>9.83</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>14.88</td>
<td>0.574</td>
<td>0.936</td>
<td>1.515</td>
<td>9.24</td>
</tr>
</tbody>
</table>

* additional significant figures due to smaller standard deviations.

Table 4-5 EIS Modeled Data of the MnMoCoO Electrode for Alkaline OER with a Solution Resistance of $R_s = 0.2 \, \Omega$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\eta$ (mV)</th>
<th>$i$ (mA cm\textsuperscript{-2})</th>
<th>$CPE_{dl}$* ($F_s^{-1} \cdot \Omega^{-1}$)</th>
<th>$R_{ct}$*10\textsuperscript{-2} (\Omega)</th>
<th>$C_p$*10\textsuperscript{-2} ($F_s^{-1} \cdot \Omega^{-1}$)</th>
<th>$R_p$* ($\Omega$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnMoCoO</td>
<td>250</td>
<td>0.61</td>
<td>1.521</td>
<td>0.885</td>
<td>2.948</td>
<td>7.18</td>
</tr>
<tr>
<td></td>
<td>275</td>
<td>1.56</td>
<td>1.294</td>
<td>0.900</td>
<td>2.853</td>
<td>7.42</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>4.04</td>
<td>1.066</td>
<td>0.915</td>
<td>2.632</td>
<td>8.09</td>
</tr>
<tr>
<td></td>
<td>325</td>
<td>10.41</td>
<td>0.839</td>
<td>0.931</td>
<td>2.227</td>
<td>10.12</td>
</tr>
</tbody>
</table>
The best MEMD electrode in terms of overpotential is MnMoVO. This electrode when compared to the EMD control and other electrode samples, shows a lower intensity and broad peaks corresponding to 021 and 002. This indicates a change in the crystalline structure from that of the starting EMD. All samples show different crystalline structures based on differences in their 021 and 002 peaks. It is difficult to explain improvements in overpotential based on crystalline structures. Deciphering the catalytic properties of a material for a reaction could be straight forward in some circumstances and challenging in others. There are three basic concepts to explain reaction rates: collisions, energy barrier and the geometry of the collision. In this respect, the modification of the crystalline structure of γ-MnO₂ (EMD) as in the case of the MnMoVO sample is believed to be one of factors lowering its alkaline OER overpotential.

4.4.4 XPS Spectra

The γ-MnO₂ (EMD) can be described by the chemical formula\(^{17}\) as:
\[ \text{Mn}_{1-x-y}^4\text{Mn}_y^{3+} \text{O}_{2}^{2-}_{\frac{2}{2} - 4x - y} \text{OH}_{4x + y}^{-} \]

Where \( x \) is the cation vacancy fraction and \( y \) is the fraction of \( \text{Mn}^{3+} \) ions, replacing \( \text{Mn}^{4+} \) in the manganese sub-lattice. EMDs have typical values of \( x \) and \( y \) as follows: \( x \approx 0.06 \) and \( y \approx 0.075 \). This means that \( \text{Mn}^{4+} \) should be the dominant specie in EMDs.

Fig. 4-4 shows the X-ray photoelectron spectroscopy of the EMD based electrodes. To analyze these results, peak fitting parameters from \( \text{Mn}(2p) \) and \( \text{O}(1s) \) have been taken from Nesbitt\(^{18} \). It is possible to elucidate some differences in composition of manganese oxidation states, water content and oxygen electron acidity by comparing the XPS spectra between samples. These variables can be correlated to the overpotential toward alkaline OER of the samples to find trends.

Two states of manganese peaks are observed, corresponding to the \( \text{Mn}(2p_{1/2} \text{ and } 2p_{3/2}) \) spin orbit split components. Comparing the XPS results from the samples to the control sample (EMD), it can be seen that all the XPS spectra of these samples have similar \( \text{Mn}(2p) \) peak locations with the exception of \( \text{MnMoWO} \). The \( \text{MnMoWO} \) sample has \( \text{Mn}(2p) \) peaks shifted toward higher binding energies (BE) indicating a higher proportion of \( \text{Mn}^{4+} \). Additives change the ratio of \( \text{Mn}^{4+} \) to \( \text{Mn}^{3+} \) during electrodeposition. In addition, XPS peak fitting suggests a negligible concentration of \( \text{Mn}^{2+} \) in all the samples, which is in agreement with the formulation (4-5). This dispersion of Mn oxidation states within a molecular range could be beneficial towards the OER as the transition stage can have a lower energy profile.
because the geometry of the active site with the transition specie would require lower energy of activation.

Fig. 4 XPS Spectra of the MEMD Electrodes. Mn(2p) and O(1s) Labeled as (a) and (b), Respectively. Control Sample has been Included as Number 5.

O(1s) XPS spectra of the samples show a single peak which can be interpreted as the addition of three different chemically bonded oxygen. Considering the O(1s) peak parameters from Manganite\textsuperscript{18}, O\textsuperscript{2-}, OH and H\textsubscript{2}O peaks are found at 529.6,
530.8 and 531.6 eV, respectively. O$_2^-$, OH$^-$ and H$_2$O are structural species, although water could be adsorbed (i.e. chemically or physically). By comparing the O(1s) XPS spectra of the samples including the EMD control sample, it can be seen that all the peaks are similar with the exception of that from MnMoWO. The MnMoWO O(1s) XPS spectrum is broad and shifted toward higher binding energy (eV), indicating a higher proportion of oxygen in the form of water, which could be detrimental for the OER in terms of overpotential as it decreases electrical conductivity of the coating and lowers the quantity of active sites. The more structural water in MnO$_2$, the less active sites for electrochemical activity. This reasoning is supported by studies on EMD done by Ruetschi$^{17a}$, which is indicated that structural water content within the EMD influences its electrical conductivity.

The best EMD based sample in terms of overpotential is MnMoVO, and it shows a O(1s) XPS spectrum which is sharp and peaks at about the same location as the other samples. This result can be interpreted as low water content; in addition the O$_2^-$ peak location of MnMoVO is believed to have acid qualities in terms of how strong the outermost electrons are hold. This oxygen acidity makes it easier to accept electrons and this is important as structural oxygen is considered to become active sites. A solid acid catalyst will favorably react with a base than an acid. This could complete the explanation of why MnMoVO show improved overpotentials for alkaline electrolysis.

**4.4.5 SEM Micrographs Associated with Elemental Analysis**

Microscopic representation of the modified EMDs are compared with the conventional anodes (i.e. dimensionally stable anodes). Fig. 4-5 shows the SEM
cross-sectional and plan views of the DSA®. These images show the core Ti and IrO$_2$ coating and no TiO$_2$ in the cross-sectional view of the electrode. The DSA® layer has a thickness at about 50 to 60 μm and show porosity at the micron scale.

Fig. 4-5 SEM Micrographs of the Dimensionally Stable Anode. From left to right, Cross-sectional and Plan Views of the DSA® Electrode, Respectively.

Fig. 4-6 shows the SEM micrographs of the modified EMD electrodes in a plan view. The images show that all EMD based samples have a structure similar to that from dry mud. SEM micrographs show some relation between the grain size of the samples and their maximum roughness factors determined by EIS. Smaller grain sizes would increase the area of the cracks and oxygen can evolve along these cracks, however it should be taken into consideration that oxygen in the form of structural water within the MEMD lowers the quantity of active sites.

Elemental analysis of the electrodes analyzed by EDS technique is shown in Table 4-6. In addition to the results from XPS, one can infer some correlation between the water content and the improvement in overpotential found among the electrodes. Among the various additives studied the MnMoVO electrode in particular show a substantial decrease in oxygen content which is attributed to low
water content. Low water content is beneficial as the electrical conductivity of the coating increases.

![SEM Micrographs of the MEMD Electrodes](image)

**Fig. 4-6 SEM Micrographs of the MEMD Electrodes:** (1)MnMoVO; (2)MnMoWO; (3)MnMoCoO; and (4)MnMoO.

<table>
<thead>
<tr>
<th>Concentration by mass (%)</th>
<th>Sample ID</th>
<th>MnMoVO</th>
<th>MnMoWO</th>
<th>MnMoCoO</th>
<th>MnMoO</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>11.76</td>
<td>20.00</td>
<td>12.88</td>
<td>53.28</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>71.82</td>
<td>63.28</td>
<td>63.27</td>
<td>32.10</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>14.92</td>
<td>12.33</td>
<td>20.32</td>
<td>14.62</td>
<td></td>
</tr>
<tr>
<td>V/W/Co</td>
<td>1.50</td>
<td>4.38</td>
<td>3.53</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>

### 4.5 Conclusions

A proof of concept for modified electrolytic manganese dioxide (MEMDs) has been accomplished through electrochemical and surface studies. There are two
directions in improving EMD toward alkaline OER, higher roughness factor and low water content have shown certain correlation to alkaline OER overpotential improvement. In addition, structural O$^{2-}$ acidity is believed to influence overpotential to some extent. Roughness factor and water content have been determined by EIS, XPS and EDS, respectively. It is believed that further improvement in overpotential is achievable. If a material can be developed with a competitive overpotential toward alkaline OER then it would be a more cost-effective option than conventional DSA® anodes.

4.6 References


10. Ji-Ming Hu; Jian-Qing Zhang; Cao, C.-N., Oxygen Evolution Reaction on IrO$_2$-based DSA$^\text{®}$ Type Electrodes: Kinetics Analysis of Tafel Lines and EIS. *Int. J. Hydrogen Energ.* **2004**, *29*, 791-797.


Chapter 5

5 Co/Mo Bimetallic Addition to Electrolytic Manganese Dioxide for Oxygen Generation in Acid Medium

5.1 Introduction*

Hydrogen is an abundant, renewable and clean energy source and has been considered as a solution to the problems arising from the current unsustainable fossil fuel economy. Recently, the hydrogen economy is gaining the attention of government bodies and major oil companies\(^1\). Hydrogen can be generated through various methods including thermochemical, electrochemical and biochemical\(^2\). Of all these available methods, water electrolysis (via electrochemical) is suitable for large scale production of hydrogen. Electrolysis of water is a simple way to produce hydrogen with high purity at an economical price when a source of energy to drive the electrolysis is available such as solar or nuclear energy\(^3\).

The water electrolysis consists of two electrochemical reactions, termed as hydrogen and oxygen evolution reactions (HER and OER). The equilibrium potential of water electrolysis is 1.23 V at standard conditions but to drive the electrolysis at a practical rate requires higher potentials and this is conventionally measured as overpotential\(^2\). The difference between the equilibrium potential and the potential at

practical current densities (e.g. 100 mA cm\(^{-2}\)) is called polarization or overpotential (\(\eta\)). Metals such as Pt and Ru provide an excellent catalytic surface in lowering the overpotential (\(\eta\)) for the HER\(^4\). The most notable catalysts belong to the platinum group metals and are used for the HER, in addition, platinum group oxides\(^5\) are used for the OER. However, platinum group metals are greatly limited by its scarcity and high cost. For instance, technologies such as fuel cells cannot be scaled up because they require expensive catalyst. The most efficient electrocatalyst for the OER are metal oxide electrodes\(^5b,sc\) (RuO\(_2\) being the best\(^sc\)). Oxides present advantages over metal counterparts because they are more stable and cannot be further oxidized. Hence, the desire is to develop an inexpensive noble metal free OER catalyst.

With this as an objective, in this chapter, the use of electrolytic manganese dioxide (EMD, \(\gamma\) type MnO\(_2\)) with in-situ addition of cobalt/molybdenum ions during electrodeposition (termed modified EMD) has been investigated as a potential catalyst towards the OER. The modified EMD significantly lowers the overpotential of the parent EMD material. Another objective of this work is to investigate the reasons for the decrease in overpotential found with these electrodes while varying the Co content in the bath solution. To the best of our knowledge, modified EMD (MEMD) materials with Co as an additive have not been reported previously. Electrolytic manganese dioxides are a well-researched area in energy storage\(^6\) as well as for catalysts to suppress the chlorine evolution reaction\(^7\) in seawater electrolysis. These studies support the concept of this material for electrochemical applications.
EMD is brittle and adding molybdenum has been found to improve its adherence to the substrate\(^7\). Besides molybdenum, a range of other additives in the electrolytic bath have also been investigated\(^7\) in the range of 3 to 9 mM in the electrolytic bath. However, the cobalt additive in EMD is little known or not well established and we have used this additive in the range of 3 to 15 mM. The role of cobalt as an additive in MnO\(_2\) has different advantages in terms of lowering water content and improving the conductivity that improved the energy efficiency which is discussed in the current study. The combination of molybdenum and the extent of higher amount of cobalt in the bath, appears to be beneficial for the OER as determined in the present chapter. In the design of catalysts for ammonia synthesis, the combination of Co/Mo has been both, experimentally and theoretically reconciled\(^8\), and found to outperform ruthenium (platinum group element). The current novel trend for catalyst design is the combination at the molecular scale of elements (e.g. Mo and Co) which show low and high bond strength with reaction intermediates, to generate intermediate bond strength and this is the region where catalysts operate more efficiently\(^8\).

In the previous chapter, I have reported MEMD for the OER in alkaline medium\(^9\), where a range of doping elements were investigated. The reported doping elements enhanced the overpotential at a current density of 100 mA cm\(^{-2}\). Whereas in the current chapter, these developed MEMD materials showed a competitive overpotential when used in acid medium, as opposed to our previous work in chapter 3 reported for alkaline medium\(^9\). It should be noted that the overpotential at a current density of \(\eta_{10}\) 10 mA cm\(^{-2}\) has recently received more attention as it is believed to be a representative variable for water splitting devices. However, we have used the
conventional $\eta_{100}^2$ and found the results to be promising. The significance of this work, as determined in this chapter lies in the technological improvement in electrode performance when acid medium is the electrolyte.

5.2 Theory

Delgado et al$^2$ shows different OER mechanisms, of all these proposed mechanisms, the one selected to fit the data is that used by Da Silva et al$^{10}$. This mechanism path is described by the following steps (M refers to the active site):

\begin{align*}
M + H_2O & \rightarrow M - OH_{\text{ads}} + H^+ + e^- \quad 5-1 \\
M - OH_{\text{ads}} & \rightarrow M - O_{\text{ads}} + H^+ + e^- \quad 5-2 \\
M - O_{\text{ads}} & \rightarrow M + \frac{1}{2}O_2 \quad 5-3
\end{align*}

Hu$^{11}$ determined a slope of 59 mV and 130 mV for the OER on DSA in acid media. He employed the previous mechanism (i.e. Eqs. 5-1 to 5-3) to reconcile EIS data at low overpotentials. However, a modification to the first OER step (i.e. Eq. 5-1) has been done by dividing it into two sub-reactions$^{11}$ to account for a Tafel slope of 59 mV dec$^{-1}$:

\begin{align*}
M + H_2O & \rightarrow M - OH^*_{\text{ads}} + H^+ + e^- \quad 5-4 \\
M - OH^*_{\text{ads}} & \rightarrow M - OH_{\text{ads}} \quad 5-5
\end{align*}

Where $M - OH^*_{\text{ads}}$ and $M - OH_{\text{ads}}$ are adsorption intermediates with the same chemical structure but different energy states. By including $O_{\text{ads}}$, there are two different chemical structural adsorbed species. Similar mechanism has been
proposed by other authors\textsuperscript{10, 12}. Hu et al\textsuperscript{11} experimentally showed that the coverage of $O_{ads}$ is substantially lower than both, $OH^*_{ads}$ and $OH_{ads}$ and it is close to zero. Hu\textsuperscript{11} modeled his EIS data with a modified 1CPE circuit as shown in Fig. 2-9 (in chapter 2). These results support the use of an equivalent electrical circuit for one adsorbate.

5.3 Materials and Methods

5.3.1 Electrode Preparation

The electroplating station consisted of the plating solution, a power supply and electrodes; one 70 x 50 x 1 mm 316 stainless steel sheet, and one 20 x 10 x 1 mm IrO$_2$/Ti sheet (DSA\textsuperscript{®} acquired from AMAC Corrosion Co.) with one face insulated by ferro-lacquer, as counter and working electrodes, respectively. An internal half-cell vessel connecting the solutions by a Nafion membrane was used. The solutions used in the preparation of modified EMDs are tabulated in Table 5-1. The samples were electrodeposited at $i = 10$ mA cm$^{-2}$. The samples were dried at 100 °C in an oven for a period of 1 hour in an air atmosphere as the last preparation step.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Reagents (Analytical grade)</th>
<th>Concentration g l$^{-1}$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnMoO and MnMoCoO # 1 / 2 / 3 / 4 / 5</td>
<td>90</td>
<td>20</td>
<td>MnSO$_4$· 5H$_2$O</td>
<td>33.802</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Na$_2$MoO$_4$· 2H$_2$O</td>
<td>0.726</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H$_2$SO$_4$</td>
<td>42.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CoSO$_4$· 7H$_2$O</td>
<td>0/0.843/1.687</td>
<td>7a	extsuperscript{d}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.795/5.060/6.325</td>
<td></td>
</tr>
</tbody>
</table>

5.3.2 Linear Voltammetry (LV)

A three electrode set up, remotely controlled by a BioLogic VSP potentiostat was used. The reference (RE) and counter electrode (CE) were Ag|AgCl satd. KCl and a
platinized platinum sheet with the dimensions of 10 x 10 x 1 mm, respectively. EMD based electrodes were made anodic in 2 M H₂SO₄ solutions in the OER regime. The scan rate was 0.1 mV s⁻¹ and the scan range was set arbitrarily from low to high current density in the vicinity of 100 mA cm⁻². The IR drop compensation was carried out by the current interruption method. The potential of the Ag|AgCl sat. KCl electrode was taken as 197 mV vs. SHE. Finally, the geometric or apparent area of the coating was used in the determination of current densities and all the tests were done at 25 °C.

5.3.3 Electrochemical Impedance Spectroscopy (EIS)

EIS is performed over the frequency range from 10 kHz to 0.05 Hz performed sequentially at potentials in the OER regime. The ac sinusoidal voltage applied had an amplitude of 5 mV at 25°C. A fit for purpose argentia satd. KCl RE was used for this test.

5.3.4 Surface Tests

The crystallinity of the deposits was examined by a Siemens X-ray diffractometer with Philips Co-Kα radiation (1.7902 Å). X-ray photoelectron spectroscopy (XPS) was used to examine the chemical structures in the deposits with a Thermo Multilab 2000. Carbon, C(1s), was used as the reference spectrum. Finally, the morphology of the deposits was determined by field emission scanning electron microscopy (FE-SEM) and a SEM equipped with energy dispersive analysis (EDS) for qualitative elemental analysis using two JEOL instruments, models JSM-7000F and JSM-6000, respectively. EMD was used as reference and labeled EMD control; this sample was used for XRD and XPS tests.
5.4 Results and Discussions

5.4.1 Tafel Plots

Figure 5-1 shows the Tafel plot of the modified EMD samples with Co and Mo as additives (MnMoCoO) for the OER in 2 M H₂SO₄ solution. For all the samples tested, the Tafel lines show one slope close to ~ 60 mV dec⁻¹ in the low current density region and another slope at around ~ 115 mV dec⁻¹ in the high current density region. In the theory (section 5.2) it is explained the OER mechanism steps that reconcile the different Tafel slopes found. A change in the magnitude of the Tafel slope indicates different rate determining steps (rds) which can be related to those proposed by different sources⁴⁻⁵. In the OER region the electrodes with varying Co content exhibit different values of overpotential.

Table 5-2 shows the electrochemical parameters of all the tested samples. Among the modified samples studied, the sample with the highest cobalt concentration labelled #5 (i.e. MnMoCoO #5) exhibits the best overpotential (i.e. 305 mV) when
compared to that from DSA® at 100 mA cm$^{-2}$ (i.e. 341 mV). DSA® has been reported to have similar overpotentials ($\eta$) and Tafel slopes ($b$) to those determined by other research groups$^{5a,11}$. Hu et al reported$^{11}$ that the oxygen evolution reaction on IrO$_2$ based DSA® electrodes to have Tafel slopes of 59 mV dec$^{-1}$ and 130 mV dec$^{-1}$ at low and high overpotentials, respectively. Similar slopes have been determined. At low overpotentials the rate determining step (rds) is that described by Eqs. 5-4 and 5-5. For high overpotentials the rds is described by the Eq. 5-1 as it yields a slope of 120 mV dec$^{-1}$.

Table 5-2 Experimental Electrochemical Parameters of the Samples for the OER in 2 M H$_2$SO$_4$.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$b$ (mV dec$^{-1}$)</th>
<th>$\eta_{100}$(mV)</th>
<th>$\log(i_o)^*$ (mA cm$^{-2}$)</th>
<th>$R_{ct}^*$ at $\eta_{10}$ (Ω cm$^2$)</th>
<th>$r_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnMoCoO #5</td>
<td>59</td>
<td>305</td>
<td>3.34</td>
<td>0.290</td>
<td>429</td>
</tr>
<tr>
<td>MnMoCoO #4</td>
<td>65</td>
<td>319</td>
<td>2.68</td>
<td>0.256</td>
<td>630</td>
</tr>
<tr>
<td>MnMoCoO #3</td>
<td>62</td>
<td>306</td>
<td>3.76</td>
<td>0.475</td>
<td>379</td>
</tr>
<tr>
<td>MnMoCoO #2</td>
<td>61</td>
<td>346</td>
<td>3.31</td>
<td>0.191</td>
<td>645</td>
</tr>
<tr>
<td>MnMoCoO #1</td>
<td>61</td>
<td>364</td>
<td>3.42</td>
<td>0.315</td>
<td>394</td>
</tr>
<tr>
<td>DSA</td>
<td>51</td>
<td>341</td>
<td>3.87</td>
<td>0.267</td>
<td>388</td>
</tr>
</tbody>
</table>

*: Rounded up values based on their standard deviations.

The performance characteristics of the MnMoCoO samples have been substantially improved by adding CoSO$_4$ in the plating solution (see Fig. 5-1 and Table 5-2). The overpotential of the modified EMD samples in Table 5-2 for acid electrolyte is found to be superior to those reported from our previous work$^9$ in alkaline electrolyte. A change in the electrolyte, yields different types of adsorbed reaction intermediates (i.e. Eqs. 5-1 to 5-5). The bond strength between the catalyst surface and an adsorbed reaction intermediate, changes as a function of the adsorbate chemical structure and this could be the reason of the changes seen in the results for the overpotential found in the OER in different electrolytes. In this respect, other
variables such as the exchange current density ($i_0$) and charge transfer resistance ($R_{ct}$) ($R_{ct}$ is explained in chapter 2, section 2.5.1.2) do support the results found by Tafel slopes in Fig. 5-1. These variables ($i_0$, $R_{ct}$) from the MEMD samples show better values to those from DSA® (see Table 5-2).

### 5.4.2 Electrochemical Impedance Spectroscopy

The equivalent circuit selected to model the EIS data is the 1CPE model. The modified 1CPE model was not considered because SEM/EDS analysis determined no TiO$_2$ between the DSA® and the Ti substrate (refer to section 4.4.5 in chapter 4). This selection is further explained in our previous work about MEMD$^9$, where we neglected the impedance of the coatings for the EIS analysis.

Fig. 5-2(a) shows the Nyquist impedance and 5-2(b) Bode admittance diagrams of the best performed sample (i.e. MnMoCoO #5) to illustrate intermediate data processing results. The curves shown in Fig. 5-2 are representative for all the MnMoCoO samples studied, which exhibit one capacitive loop that has been interpreted to be related to kinetic control$^{13}$. No other capacitive or inductive loops corresponding to mass transfer control or oxide impedance are identified. Variables of importance from the 1CPE model are the $CPE_{dl}$ and $R_{ct}$, as they provide direct information about the roughness factor and energy efficiency. The charge transfer resistance ($R_{ct}$) was determined at a current density of 10 mA cm$^{-2}$ and this variable is close to that of the DSA® sample. The results are tabulated in Table 5-2. $R_{ct}$ is believed to directly correlate to overpotentials for the OER, as oppose to a high roughness factor, which not necessarily means that the overpotential ($\eta$) will improve. Average roughness factors ($r_f$) have been determined by Eq. 2-32 (in chapter 2) and the corresponding values are tabulated in Table 5-2. Roughness
factors have been determined to be in the same order of magnitude for all the samples, including the DSA®.

Fig. 5-2 (a) Nyquist Impedance and (b) Bode Admittance Diagrams of the MnMoCoO #5 Sample at $\eta = 245$ mV in 2 M H$_2$SO$_4$ Solution. Continuous Lines Represent the Fitted Curve by the 1CPE Model, Experimental Data as Symbols.
5.4.3 XRD Spectra

EMDs in general are mainly composed of $\gamma$-MnO$_2$ and to a small extent by $\epsilon$-MnO$_2$\textsuperscript{14}. $\gamma$-MnO$_2$ is composed of pyrolusite and ramsdellite, they both have a 110 line, however $\epsilon$-MnO$_2$, does not. EMDs have the 021 line with the highest intensity followed by the 110 line\textsuperscript{14b}. Fig. 5-3a shows the X-ray diffraction spectra of the MEMD samples. The control sample and substrate are included in order to study the degree of changes in the crystallinity. Identifiable peaks are indicated on the control sample as 021, 002. The 110 peak in the EMD control sample is represented as 110*, as the substrate exhibits a peak at the same region, therefore this peak has not been considered for further the analysis.

For the samples with increasing cobalt additive, labeled # 1 to # 5 (#5 being the sample with the highest addition of Co, for details refer to Table 1) the XRD spectra show similar peaks to that of the control sample. As the content of cobalt in the EMD solution increases, the (002) peak intensity decreases. However, the (021) peak remains constant but becomes broad. The observed changes in the crystallinity of the samples could be one of the beneficial factors towards improved overpotential for oxygen generation. To study the chemical stability of the MEMD samples, the sample #5 is selected (best energy efficient sample towards the OER). We have performed XRD analysis before and after electrochemical measurements to determine any changes in the crystalline structure. Fig. 5-3b shows the XRD spectra of the MnMoCoO #5 sample, before and after electrochemical measurement. As observed from the XRD (Fig. 5-3b) the diffraction patterns are almost identical, indicating no changes in the crystalline structure. This confirms that modified EMD is chemically stable for the acid OER regime.
Fig. 5-3 (a) X-ray Diffraction Patterns (XRD) of the Modified EMD Samples. (b) XRD of the MnMoCoO #5 Sample (Best Energy Efficient Sample) Before and After Electrochemical Measurements Indicating the Stability of the EMD Structure.

Deciphering the catalytic properties of a material for a reaction could be straightforward in some circumstances and challenging in others. There are three basic concepts to explain reaction rates: collisions, energy barrier and the geometry of the
collision. In this respect, the modification of the crystalline structure of γ-MnO₂ (EMD) is believed to be one of the factors lowering its OER overpotential.

5.4.4 XPS Spectra

The γ-MnO₂ (EMD) can be described by the chemical formula\(^{15}\) as:

\[
\text{Mn}^{4+}_{1-x-y}\text{Mn}^{3+}_y\text{O}^{2-}_{2-4x-y}\text{OH}^-_{4x+y}
\]

Where \(x\) is the cation vacancy fraction and \(y\) is the fraction of Mn\(^{3+}\) ions, replacing Mn\(^{4+}\) in the manganese sub-lattice. EMDs have typical values of \(x\) and \(y\) as follows: \(x \approx 0.06\) and \(y \approx 0.075\). This means that Mn\(^{4+}\) should be the dominant specie in EMDs.

Fig. 5-4 shows the X-ray photoelectron spectroscopy (XPS) of Mn(2p) and O(1s) for the samples. Two types of manganese (Mn) peaks are observed, corresponding to the Mn(2p\(_{1/2}\) and 2p\(_{3/2}\)) spin orbit split components. Comparing the XPS results from the samples to the control sample, it can be seen that all the XPS spectra of these samples are similar to the control sample. This result suggests that the ratio of Mn\(^{4+}\) to Mn\(^{3+}\) in the MEMD remains constant despite of increasing the concentration of Co\(^{2+}\) ion in the plating solution.
Fig. 5-4 XPS Spectra of the Modified EMD Samples. (a) Mn(2p) and (b) O(1s) Spectra. A Standard (Control) EMD Sample has been Included as Number 1.

Fig. 5-4b also shows the O(1s) XPS spectra of the samples. Considering the O(1s) peak parameters from Manganite\textsuperscript{16}; O$^{2-}$, OH$^{-}$ and H$_2$O peaks are found at 529.6, 530.8 and 531.6eV, respectively. O$^{2-}$, OH$^{-}$ and H$_2$O are structural species. This information is used for the interpretation of the results shown in Fig. 5-4b.
Comparing the O(1s) XPS spectra of the samples to the EMD control sample, it can be seen that the EMD control spectra has a shoulder in the region of structural water, other samples do not show this shoulder. In addition, the more Co$^{2+}$ ion in the plating solution the more intense is the O(1s) peak. One could interpret these results as a decrease in water concentration that would increase the structural oxygen content in the MEMD coating. The presence of additives (i.e. Co$^{2+}$ ion) in the plating solution could be suppressing structural water formation during electrodeposition. These results indicate a lower concentration of structural water in the samples than that from the control EMD, which is beneficial for catalytic activity as it increases electrical conductivity and the quantity of active sites.

An additional figure has been included to analyze the chemical stability of the MEDM under the electrochemical test conditions. Fig. 5-5 in combination with Fig. 5-3b, show the chemical structure of the MnMoCoO #5 sample, before and after cyclic voltammetry. Figs. 5-5 and 5-3b indicate that the sample #5 is stable for the OER in acid medium.

**5.4.5 Micrographs and Elemental Analysis FE-SEM / SEM EDS**

Fig. 5-6 shows the plan micrograph view of the modified EMD samples (DSA® is shown$^9$) at low and high magnifications. These results show that all EMD based samples have a structure similar to that of dry mud. SEM results show an increase of the dry mud polygon size when the Co$^{2+}$ content in the plating solution is increased when compared to the standard EMD. The SEM micrographs do not show a clear trend about the polygon average area enclosed by cracks as a function of Co$^{2+}$ content in the plating solution. Bigger polygon sizes would decrease the area of the
cracks and surface, this should decrease the roughness factor and hence increase the overpotential. Fig. 5-6g also compares the surface morphology of the MnMoCoO #5 after electrochemical measurements. It is visualized from the micrograph that the morphology is quite similar, indicating that the sample is mechanically stable.

![XPS Spectra](image_url)

Fig. 5-5 XPS Spectra of the MnMoCoO #5 Sample Before and After Cyclic Voltammetry. Mn(2p) and O(1s) Labeled as (a) and (b), Respectively.
Fig. 5-6 SEM Imaging of the Modified EMD Samples. (a, c and e) Refers to MnMoCoO #3, MnMoCoO #4 and MnMoCoO #5 (Low Magnification) and (b, d and f) Refers to the Respective Samples at High Magnification. Fig. 8 (g) Refers to MnMoCoO #5 After Electrochemical Measurement Showing a Similar Morphology to that of Fig. 8 (f) as Deposited Sample.
Considering the analysis from XPS and SEM/EDS (Table 5-3), it is found that the more Co\(^{2+}\) ion content in the plating solution, the lower the water content in the modified EMD electrodeposited samples. It is believed that water in the modified EMD sample does not become an active site, and its presence lowers the quantity or energy efficiency of the active sites. The electrochemical tests (i.e. Tafel plots and EIS) are closely related to electroactive area which does not have to be the same as the total area (i.e. true area). Water takes space of the surface of the electrode material, which can make the \(R_{ct}\) higher or decrease \(r_f\) depending on whether water becomes or not an active site. It can be seen that Co\(^{2+}\) content in the solution influences the composition of the coating. The higher the Co\(^{2+}\) content the less oxygen is found in the coating and this is in agreement with the results found by XPS, where water content in the modified EMD coating is lowered by Co\(^{2+}\) in solution. This is beneficial as the electrical conductivity of the coating is inversely proportional to water content. In addition, the water content lowers the quantity of active sites, making the material less electroactive.

Table 5-3 SEM EDS Elemental Analysis by Mass of the Modified EMD Coatings.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Concentration by mass (%)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O</td>
<td>Mn</td>
<td>Mo</td>
<td>Co*</td>
</tr>
<tr>
<td>MnMoO</td>
<td>53.28</td>
<td>32.10</td>
<td>14.62</td>
<td>--</td>
</tr>
<tr>
<td>MnMoCoO #1</td>
<td>25.77</td>
<td>51.77</td>
<td>22.46</td>
<td>0.00</td>
</tr>
<tr>
<td>MnMoCoO #2</td>
<td>12.88</td>
<td>63.27</td>
<td>20.32</td>
<td>3.53</td>
</tr>
<tr>
<td>MnMoCoO #3</td>
<td>16.43</td>
<td>61.58</td>
<td>21.71</td>
<td>0.28</td>
</tr>
<tr>
<td>MnMoCoO #4</td>
<td>7.35</td>
<td>79.72</td>
<td>12.64</td>
<td>0.29</td>
</tr>
<tr>
<td>MnMoCoO #5</td>
<td>5.65</td>
<td>81.25</td>
<td>12.77</td>
<td>0.33</td>
</tr>
</tbody>
</table>

*FE-SEM EDS did not detect Cobalt.

5.5 Conclusions

The current work on oxygen generation suggests that the Co/Mo addition in EMD electrodes played a crucial role. Modified electrolytic manganese dioxide
shows a competitive overpotential (305 mV) to that of traditional high-cost DSA® electrodes (341 mV) in acid OER at 100 mA cm$^{-2}$ and this is supported by electrochemical measurements. The Co$^{2+}$ ion additive directly influences the structure of MnO$_2$ thus lowering the overpotential for the OER. Among the samples studied in varying the cobalt content, the MnMoCoO #5 sample, is found to be the best in terms of energy efficiency in acid OER than DSA®. The proposed explanation about the lowering of the OER overpotential found in the modified EMD samples can be related to improved combinations of charge transfer resistance and roughness factor. In particular, the charge transfer resistance correlates directly to overpotentials. XPS and EDS show that lowering the water content in the coating increases electrical conductivity, which saves energy.

5.6 References


Chapter 6

6 Electrochemical Impedance Spectroscopy Studies on Hydrogen Evolution from Porous Raney Cobalt in Alkaline Solution

6.1 Introduction*

Recently, hydrogen has received increased attention from major oil companies like Exxon Mobil\(^1\), Shell\(^2\) and BP\(^3\). Hydrogen is a source of energy to support society. These oil companies, in their energy outlook reports, point out a more diversified future for energy supply mix in which hydrogen participates to a large extent. The energy outlooks for 2030 made by Exxon Mobil and BP indicate emerging alternative sources of energy. The Shell energy outlook speculates hydrogen fuel cell vehicles (FCVs) will compete with electric vehicles in 2050, implying that the hydrogen technology could dominate the market of transportation. Iceland, which has important sources of geo-thermal energy, generates hydrogen electrolytically, this process being powered by renewable energy. The Shell Company has supported the development of this technology in Iceland. Most of its generated hydrogen supplies the demand of the transportation sector. This is an important example that asserts successful application of this technology in a society.

Electrolytic hydrogen generation is energy intensive and expensive. Conventional materials for water electrolysis belong to the platinum group metals

\*This chapter has been accepted published as D. Delgado, M. Minakshi and D.-J. Kim “Electrochemical impedance spectroscopy on hydrogen evolution from porous Raney cobalt in alkaline solution” *Int. J. Electrochem. Sci.* 10(11) 9379-9394.
that are expensive. In this respect, our current work focuses on developing alternative electrode materials to substitute those of which are conventionally used now. Cobalt and nickel are alternative materials as they are less expensive and electrochemically active toward the hydrogen evolution reaction (HER)\(^4\). There are two approaches in improving the electrochemical activity of materials, these are known as the ‘geometric’ and ‘electronic’ factors\(^5\). Cobalt and nickel in the form of powder alloys with aluminum or zinc are called Raney after activation. Raney cobalt or nickel, has a high geometric factor as its surface area per unit of mass is substantially higher than the pure material itself. Raney cobalt and nickel were initially developed for organic reactions as catalysts\(^6\). The synthesis of Raney Co and Ni for electrode applications differs from that used for organic reactions\(^6\)\(^-\)\(^7\). The most common synthesis for Raney Co and Ni is by electrodeposition, where the powder alloy is deposited on the surface of an electrode along with Ni from the plating bath (i.e. acting as the binder), then it is activated.

Watts bath is the most common plating solution used for the purpose of depositing powder alloys\(^8\). In our current work, we have employed and reported a “modified version” of the Watts bath\(^9\). The Raney Co electrodes electrodeposited by the modified Watts bath are evaluated to determine their energy efficiency (refer to “Joule’s effect”) toward the HER in alkaline medium. In addition, the electrochemical impedance spectroscopic (EIS) technique gives useful information about how the energy is being consumed (i.e. size of the electric resistance) and EIS data is interpreted with linear voltammetry. The challenging issue is EIS data fitting, particularly when the binder competes with the catalyst (i.e. Raney cobalt or nickel). The electrochemical impedance analysis and the improved overpotential for the
electrodeposited Raney Co and Raney Co/Ni mix are reported here. Further to this, the influence of the catalyst surface roughness and its effect in energy efficiency is also detailed in this work.

It is reported by Hitz\textsuperscript{10} that Raney Ni/Al and Ni/Zn electrodes exhibited overpotentials ranging from -268 to -521 mV at a current density 100 mA cm\textsuperscript{-2} at 25 °C in 1 M NaOH. In the case of a nickel plate an increase in overpotential to -530 mV is reported\textsuperscript{11}. Further improvement in the overpotential has also been reported\textsuperscript{8, 12} well below -100 mV, however, this has been achieved only at a higher temperature of 90 °C. It is generally accepted that a decrease in ~20 mV of overpotential is reasonable, for every 10 °C of increase in temperature in the alkaline solution. The overpotentials identified from our work on Raney Co which presented here are competitive to those published earlier\textsuperscript{10} for this specific type of material.

To the best of my knowledge, no work has been reported on the use of Raney Cobalt in modified Watts bath for the hydrogen evolution reaction. A brief theory of the hydrogen evolution reaction, which commonly takes place in alkaline media during electrolysis, is given in the next section for the benefit of readers rather than solely referring to the literature.

### 6.2 Theory

Electrolytic hydrogen evolution in alkaline media has three well-known mechanism steps, described by Eqs. 6-1 to 6-3:

\[
M + H_2O + e^- \rightarrow M - H + OH^- \quad \text{6-1}
\]
\[
M - H + H_2O + e^- \rightarrow H_2 + OH^- + M \quad \text{6-2}
\]
In these Eqs., ‘M’ denotes for the active site on the catalyst and they show atomic hydrogen as the only reaction intermediate. Hydrogen can only evolve by Eqs. 6-2 and 6-3, either as a combination or by one of these two steps. When one step is rate determining (rds), discrete Tafel slope values \((b)\) are found. A Tafel slope of 120, 40 and 30 mV dec\(^{-1}\) represents Eqs. 6-1, 6-2 and 6-3 as the rds, respectively. To reconcile other slope values, modifications to the mechanism or the introduction of different isotherms are required\(^5,13\).

In addition to a Tafel slope analysis, electrochemical spectroscopy impedance (EIS) shows characteristics of the HER. EIS gives us a wide range of information, for example, there has been relevant studies about the pore shape by EIS\(^10,14\). Tafel slopes has been reconciled in terms of pore shape in some cases\(^15\). EIS equivalent circuit models for hydrogen evolution on porous surfaces have been mathematically explained in detail by Lasia\(^15-16\). The most common models used for the HER on porous surfaces such as Raney Co in alkaline medium, are shown in Fig. 2-9\(^10,16a,17\) (in chapter 2). The 2CPE model is the preferred model for data fitting for Lasia\(^10\). The 1CPE model has been used for the case of Raney Co\(^17c\), however, it is less frequently used for EIS data fitting for porous surfaces. It should be noted that the 1CPE and 2CPE models are equivalent. There is a third model that we have called 3CPE which is shown in Fig. 2-10 (in chapter 2). This model also has mathematical support and it can occur for reactions of one adsorbed specie\(^16b\).
A distinction should be made between the 1CPE and 3CPE models. The main difference between these two models is related to the magnitude of the equilibrium constants of the Eqs. 6-1 to 6-3. When the magnitude of the forward and reverse equilibrium constants of the first step (e.g. Volmer as rds) are bigger than those from the second step (e.g. Heyrovsky), one would expect the absence of inductive behavior on impedance plots. Vice versa, for instance, if Heyrovsky is the rds then a decrease in the Tafel slope should accompany the presence of an inductive loop. In the appendix B there is an explanation about the capacitive loops found for EIS data from the HER in simple terms.

Lasia has taken an estimated $C_{dl}$ of 20 $\mu$F cm$^{-2}$ for a smooth metallic electrode to determine a ratio between this value and the experimentally determined $C_{dl}$ for porous electrodes to obtain a roughness factor $r_f^{17d}$. Eq. 2-32 (in chapter 2) determines the average double layer capacitance of porous surfaces for one adsorbed specie reactions.

The parameter $T$ (in Eq. 2-32) is related to the double layer capacitance and ($T = C_{dl}$ when $\phi = 1$)$^{10}$. The variable $\phi$ is associated to an angle of depression ($1-\phi$) of the capacitive loop to account for non-idealities. Deviations from the ideal capacitance are expected as the substrate is heterogeneous; there could be lateral effects or partial transfer of charge between adsorbed molecules and the substrate$^5$. Common values of $\phi$ are found ranging from 0.75 to 0.97, on porous surfaces for the HER$^{10}$. 

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6.3 Materials and Methods

6.3.1 Electrode Preparation

The plating station consists of copper and nickel plates, acting as working and counter electrodes, respectively, a power supply, hot plate with magnetic stirrer and the plating solution. One face of the copper electrode was insulated with ferro-laque, and then it was cleaned before electrodeposition as follows. It is polished with emery paper, degreased with acetone, alkaline electrocleaned with 1.5 M NaOH solution for 1 minute at 30 mA cm$^{-2}$ at ambient temperature. Then it is acid pickled with HCl 10% for 5 seconds. After cleaning, the copper panel is plated with nickel at a current density of $i = 30$ mA cm$^{-2}$ with cobalt-aluminum and nickel-aluminum alloy particles as described by Tables 6-1 and 6-2. Raney cobalt precursor was acquired from Sigma-Aldrich in the form of cobalt-aluminum alloy powder, Co to Al ratio is 79:21 by mass. The Raney nickel particles were acquired from Merck having a composition by mass of Ni-Al 50:50. Cobalt and nickel particles are 150 micron max in size. As a safety measure, both Raney types were acquired inactive as they are pyrophoric. After deposition the coating was activated in 6.25 M NaOH solution at 70 °C for 1h.

Table 6-1 Plating Characteristics of the Raney Co Electrode.

<table>
<thead>
<tr>
<th>Solution ID</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Reagents (Analytical grade)</th>
<th>Concentration g L$^{-1}$</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>Watts Ni</td>
<td>55</td>
<td>20</td>
<td>NiSO$_4$·6H$_2$O</td>
<td>300</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NiCl$_2$·6H$_2$O</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H$_3$BO$_3$</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Watts Ni 1/2/3</td>
<td>55</td>
<td>20</td>
<td>NiSO$_4$·6H$_2$O</td>
<td>350</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NaCl</td>
<td>148/100/40</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H$_3$BO$_3$</td>
<td>30</td>
<td></td>
</tr>
</tbody>
</table>

All solutions were vigorously stirred by a magnetic stirrer.
6.3.2 Linear Voltammetry

A three electrode set up consisting of the Raney Co electrode (10 x 20 x 1 mm), platinum plate (50 x 50 x 1 mm) and Argental sat’d KCl as the working, counter and reference electrodes, respectively. These electrodes were coupled to a BioLogic VSP potentiostat to register the data. The reference electrode was placed in the vicinity of the working electrode (~2 mm) with a Luggin capillary and the $IR_{drop}$ compensation was done by the current interruption method. The alkaline medium was 2 M KOH at 25 °C. The current density range was set from 1 to 100 mA cm$^{-2}$ and the scan rate was 0.1 mV s$^{-1}$.

Table 6-2 Description of the Cobalt and Nickel Particles Coating Conditions.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Preparation</th>
<th>Raney Co or Ni concentration (g l$^{-1}$)</th>
<th>Solution ID</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Acquired</td>
<td></td>
</tr>
<tr>
<td>Raney Co 1</td>
<td></td>
<td>6.25</td>
<td>Watts Ni</td>
</tr>
<tr>
<td>Raney Co 2</td>
<td></td>
<td>12.5</td>
<td></td>
</tr>
<tr>
<td>Raney Co 3</td>
<td></td>
<td>25.0</td>
<td></td>
</tr>
<tr>
<td>Raney Co 4</td>
<td></td>
<td>25.0</td>
<td>Watts Ni 3</td>
</tr>
<tr>
<td>Raney Co 5</td>
<td></td>
<td>25.0</td>
<td>Watts Ni 2</td>
</tr>
<tr>
<td>Raney Co 6</td>
<td></td>
<td></td>
<td>Watts Ni 1</td>
</tr>
<tr>
<td>Raney Co/Ni 7</td>
<td></td>
<td>6.25*</td>
<td></td>
</tr>
<tr>
<td>Raney Co/Ni 8</td>
<td></td>
<td>12.5*</td>
<td></td>
</tr>
<tr>
<td>Raney Co/Ni 9</td>
<td></td>
<td>25.0*</td>
<td></td>
</tr>
</tbody>
</table>

*Raney Co to Raney Ni ratio 50:50 by mass.

6.3.3 Electrochemical Impedance Spectroscopy

This test was done in sequence after linear voltammetry under the same set up. EIS was done with a stabilization time between working potentials of 3 min, potential amplitude of 5 mV and a frequency range of 20 kHz to 0.05 Hz. A fit for purpose Argental sat’d KCl reference electrode was used (refer to section 7.2 in chapter 7).
6.3.4 Surface Tests

The morphology of the deposits was examined by field emission scanning electron microscopy (FE-SEM) equipped with energy dispersive analysis (EDS) for qualitative elemental analysis using a JEOL JSM-7000F SEM/EDS instrument. The crystal structure and chemical composition of the deposits were analyzed by a Siemens X-ray diffractometer with Philips Co-Kα radiation (1.7902 Å).

6.4 Results and Discussion

6.4.1 Tafel Plots

The electrochemical and kinetic parameters of the samples examined in 2 M KOH for hydrogen evolution is given in Figure 6-1 and Table 6-3. Three samples of Raney Co and three samples of Raney Co/Ni have been compared in Fig. 6-1, along with the nickel plate. Among the six Raney Co samples that have been electrodeposited (see Tables 6-1 and 6-2 for details), only three (Co 4, 5 and 6) are shown in Fig. 6-1 and the rest (Co 1, 2 and 3) are shown only in Table 6-3. Samples labeled (a) to (c) contain only cobalt particles and nickel binder. Relatively high overpotentials have been observed for the samples (a) to (c) and this has made difficult to fit impedance data, as the nickel binder (from Watts bath; see Table 6-1 for details) competes with the Raney Co particles for the HER. For this reason, fitted impedance parameters have not been processed for samples a–c. However, selected impedance spectra have been shown for these samples (in the next section 6.4.2) to illustrate differences between fitted curves and experimental points. The best samples in terms of overpotential are those which contain Raney Ni particles in the mix, these being samples (d) to (f). These mixed samples are substantially better than those with only Raney Co. This shows that Raney nickel is more active than Raney
cobalt for the HER in alkaline solution. Considering Tafel slopes, samples containing only Co particles (i.e. samples a–c) show smaller slopes at low overpotentials than those with Ni particles. This could be explained as follows.

A slope of 120 mV dec^{-1} can only be explained considering Volmer (i.e. Eq. 6-1) as the rds. Whereas, slopes of smaller magnitudes indicate Heyrovsky (i.e. Eq. 6-2) competing with Volmer. This is supported by EIS where the Raney Co 1 sample shows an inductive loop in the Nyquist diagram as shown in Fig. 6-2. Inductive loops are an indication that Heyrovsky is competing with Volmer as the rds, this was described in the theory section where the 3CPE circuit was outlined (more information is shown in section 2.5.1.2 and appendix B).

The next variable of interest is the oxygen content. Oxygen content does not affect the overpotential for the HER on Raney Co coatings, and this is different from
those results found for Raney Ni (in chapter 7). The reason for this result is the high $R_{ct}$ values found for Raney Co, which is supported by its relatively high overpotentials for the HER. Hitz$^{10}$ reported $R_{ct}$ values which are in agreement to those observed here in this work. Nickel binder with high oxygen content has shown electrical resistances ($R_f$) as large as 0.5 $\Omega$ cm$^2$ (in chapter 7). This oxide resistance is significantly smaller than the $R_{ct}$ value (14.6 $\Omega$ cm$^2$) shown for the Raney Co 6 sample at $\eta$ = −150 mV shown in Fig. 6-2. Most of the overpotentials found in the samples 1 to 6 are dominantly controlled by their $R_{ct}$, this explains why, despite of samples containing high oxygen content, their overpotentials cannot be explained in terms of the additional impedance from the oxide loop.

### Table 6-3 Experimental Kinetic Parameters of the Samples for the HER in 2 M KOH (per apparent area).

<table>
<thead>
<tr>
<th>Raney Co or Co/Ni sample ID</th>
<th>-$b$ (mV dec$^{-1}$)</th>
<th>-$\eta_{100}$ (mV)</th>
<th>$R_{ct}$* at $\eta_{10}$ ($\Omega$ cm$^2$)</th>
<th>$r_f$* at $\eta_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>low $\eta$</td>
<td>high $\eta$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>98</td>
<td>171</td>
<td>378</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>128</td>
<td>349</td>
<td>--</td>
</tr>
<tr>
<td>3</td>
<td>98</td>
<td>98</td>
<td>352</td>
<td>--</td>
</tr>
<tr>
<td>4</td>
<td>112</td>
<td>146</td>
<td>359</td>
<td>--</td>
</tr>
<tr>
<td>5</td>
<td>101</td>
<td>160</td>
<td>386</td>
<td>--</td>
</tr>
<tr>
<td>6</td>
<td>112</td>
<td>143</td>
<td>354</td>
<td>--</td>
</tr>
<tr>
<td>7</td>
<td>128</td>
<td>179</td>
<td>313</td>
<td>1.82</td>
</tr>
<tr>
<td>8</td>
<td>126</td>
<td>191</td>
<td>270</td>
<td>1.53</td>
</tr>
<tr>
<td>9</td>
<td>117</td>
<td>162</td>
<td>271</td>
<td>3.69</td>
</tr>
</tbody>
</table>

* Rounded up values based on their standard deviations.

#### 6.4.2 Electrochemical Impedance Spectroscopy Plots

Based on the facts explained in the previous section 6.4.1, we have focused our studies only on the samples (d – f in Fig. 6.1) for EIS data processing. This set of samples show lower overpotentials when compared to the other samples which contain only cobalt (a – c in Fig. 6.1). The nickel binder does not compete with the
Raney Co/Ni mix catalyst which makes a better fitting for the EIS data. However, we show selected impedances for samples Co 1 and Co 6 to describe the conflicts found when performing EIS data fitting. Figures 6-2 to 6-5 show the Nyquist impedance and Bode admittance of selected Raney samples.

Fig. 6-2 Nyquist and Bode Admittance Diagrams of the Samples 1 and 6 for the HER in 2 M KOH solution. Continuous Lines represent the Fitted Curve by the 3CPE Model for the Sample 1 and Modified 2CPE Model for the Sample 6, Experimental Data as Symbols.

Figure 6-2 compares the impedances of the Raney Co 1 and Co 6 samples. The impedance spectra for sample 1 show inductive loops, in addition to having a lower Tafel slope. The sample 1 was prepared with the smallest concentration of Co particles (i.e. 6.25 g l⁻¹) and it is the only sample which shows inductive loops. The formation of inductive loop suggests that the nickel as the binder is competing with Raney Co. Figure 6-2 also includes the impedance spectra of the sample Co 6, and it does not show any inductive behavior (absence of negative phase (Y)), while it
shows an additional capacitive loop in a frequency region where oxides could manifest. This oxide loop appears as a shoulder in the Bode admittance diagram (in Fig. 6-2) at a log of the frequency between 2 and 3. This sample shows the highest amount of oxide by EDS analysis which quantified as high as 7.83%, among all the Raney samples studied, tabulated in Table 6-4. The modified 2CPE model (i.e. an additional capacitive loop added to this model) failed to fit the experimental data of the sample 6 as most of the experimental points do not intersect the fitted curve. In Raney Co samples, when the nickel binder competes for the HER, such samples do not yield a good EIS data fitting as the Ni binder and the Co catalyst have different impedances for the HER, and hence the 2CPE model may not be suitable.

The difficulty in fitting EIS data for the samples containing only Raney cobalt is that the nickel binder competes with the cobalt catalyst and this is again demonstrated in Fig. 6-3. The data in Figure 6-3 shows that at the frequency region where the charge transfer impedance manifests, no constant slope is observed for sample 3, whereas for sample 8 a constant slope for all the cycles is shown. This indicates that there is one dominant type of interaction between one of the Raney types (i.e. nickel or cobalt) and the HER for the sample 8. This is not the case for the sample 3, which is believed that the HER occurs on a combination of the nickel binder and Raney cobalt as a function of overpotential. This combination of the HER occurs on different materials as a function of overpotential and it could explain why it is difficult to fit EIS data for the samples 1 to 6.
Samples containing Ni particles in the mix (i.e. Raney Co/Ni samples 7 to 9) show better EIS data in terms of model fitting. The EIS fits improve at higher overpotentials where Ni particles become the dominant location for the HER. At low overpotential ($\eta = -35$ mV), for sample 7, two regions corresponding to kinetic and mass transfer have been indicated\(^{18}\) in Fig. 6-4 while for high overpotential ($\eta = -150$ mV) the kinetic loop becomes dominant.

![Experimental Bode Admittance Diagram of the Samples 3 and 8 for the HER in 2 M KOH Solution.](image)

Fig. 6-3 Experimental Bode Admittance Diagram of the Samples 3 and 8 for the HER in 2 M KOH Solution.

Fig. 6-4 shows that the higher the overpotential, the better the fit for sample 8. However, the EIS data from samples 7 to 9 is difficult to fit at low overpotentials, one example is shown in Fig. 6-5 (i.e. Bode admittance at $\eta = -30$ mV). There is a region where a slight discrepancy is observed in the fit (i.e. missing a few of the experimental points). As discussed earlier, when two materials compete for the reaction then the model may not be appropriate. The CPE model series have been
developed for one type of reaction intermediate, $M - H$ as shown in the mechanism steps (Eqs. 6-1 to 6-3). In the region of interest, being around $\eta_{10}$ (cf. Fig. 6-1) the fits improve substantially as shown in Figs. 6-4 and 6-5. This supports the reasoning that Raney Ni is more active than Raney Co and the nickel binder.

Fig. 6-4 Nyquist and Bode Admittance Diagrams of the Samples 7 and 8 for the HER in 2 M KOH solution. Continuous Lines Represent the Fitted Curve by the 2CPE Model for both Samples, Experimental Data as Symbols.

**6.4.3 X-ray Diffraction Spectra**

Figs. 6-6 and 6-7 show the XRD spectra of the samples. They differ substantially in their counts (i.e. see y-axis of the Figs.) therefore they have been placed into two separate figures. All the samples show the characteristic Ni peaks and these have been indicated in the figures. The copper substrate in Fig. 6-7 shows the copper peaks and some of the samples show the copper peaks in addition to the synthetic nickel peaks.
Fig. 6-5 Nyquist and Bode Admittance Diagrams of the Sample 9 for the HER in 2 M KOH solution. Continuous Lines Represent the Fitted Curve by the 2CPE Model for both Samples, Experimental Data as Symbols.

Fig. 6-6 X-ray Diffraction Spectra of the Raney Co Samples.
No evidence of peaks belonging to other elements was found, including metal oxide present in the Raney samples in XRD spectra. Cobalt in particular was not determined by XRD; it should be noted that if the cobalt peaks were present, these would have been overlapped with the Ni peaks. After a careful analysis, no peaks relating NiO or CoO have been identified but EIS suggest that the presence of oxygen in the samples could be in the form of nickel oxide.

![X-ray Diffraction Spectra of the Raney Co/Ni Samples.](image)

It was determined that nickel-oxide species in the binder have low concentration and/or are amorphous, therefore XRD cannot find these species under these conditions. As XRD is not feasible, alternatively, we have used FE-SEM associated with EDS to analyze the oxygen content in the samples.

### 6.4.4 Field Emission Scanning Electron Microscope Analysis

Figure 6-8 shows the micrograph of the Raney Co/Ni sample 8, which is the most energy efficient for the HER (cf. Table 6-3). This is the common morphology
that is found in all the sample surfaces. Fig. 6-8 supports the use of equivalent electric circuits for porous surfaces. Table 6-4 shows the oxygen elemental dispersive analysis done by FE-SEM. High concentrations of NaCl (from the Watts bath) are detrimental for the deposition of the binder as it increases the oxygen content in the coating, and this increases its electrical resistance. The Watts bath modification by substituting NiCl$_2$·6H$_2$O with NaCl, is a satisfactory option as it decreases the oxygen content in the coating when the concentration of NaCl is 40 g l$^-1$. This is supported with results found for the sample 4 which shows the smallest percentage of oxygen.

![Fig. 6-8 FE-SEM Micrograph of the Raney Co/Ni 8 Sample.](image)

**Table 6-4 Oxygen Elemental Dispersive Analysis for the Raney Co and Co/Ni Electrodes.**

<table>
<thead>
<tr>
<th>Concentration by mass (%)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>1.70</td>
<td>5.23</td>
<td>3.98</td>
<td>0.89</td>
<td>2.16</td>
<td>7.83</td>
<td>2.14</td>
<td>2.34</td>
<td>1.13</td>
</tr>
</tbody>
</table>
The origin of oxygen species in the Raney catalyst can be explained from Pourbaix\textsuperscript{19}. It explains that the electrodeposition of nickel from a Watts bath has \(~97\%\) efficiency and undesirable side reactions such as oxide and hydroxide deposition could be expected. Similar to the Pourbaix illustration, in our next chapter 7, we have observed NiO and Ni(OH)\textsubscript{2} on the electrodeposited sample through XPS analysis. The mechanism of the formation of nickel oxide as a side reaction explained by Pourbaix is as follows:

\[
\text{Ni} + \text{H}_2\text{O} \rightarrow \text{NiO} + 2\text{H}^+ + 2\text{e}^-
\]  

In the Eq. 6-4, NiO can become hydrated NiO.\textsubscript{H}\textsubscript{2}O or form nickelous hydroxide Ni(OH)\textsubscript{2}. The free enthalpy of formation of NiO and Ni(OH)\textsubscript{2} are \(-51,300\) cal and \(-108,300\) cal, respectively. A negative free enthalpy of formation represents that the reaction is spontaneous but it does not imply that it is kinetically dominant. This supports the concept of the presence of oxide in our electrodeposited Raney samples.

The results obtained from our studies are competitive to those commonly reported for this type of material in the literature\textsuperscript{8, 10, 12}. The best overpotential observed was for the sample 8 (-270 mV) at 100 mA cm\textsuperscript{-2}, which is within the range of 200-350 mV, where most Raney type catalysts are located. Raney nickel is a better catalyst for the HER than Raney cobalt, because in addition to a high roughness factor, it is likely that nickel has a better electronic factor than cobalt. A better electronic factor is related to intermediate values of bond strength, between the active site and adsorbed hydrogen.
6.5 Conclusions

A porous Raney cobalt surface enhances the available area for the hydrogen evolution reaction to occur. The presence of porosity increases the efficiency of an electrodeposited material in comparison to cobalt having non-porous (i.e. smooth) surface. Raney Co showed a reasonable overpotential of -349 mV for the HER. However, when Raney Ni is added into the Raney Co coating, this improves the overpotential of the electrode substantially, exhibiting -270 mV. For all the Raney Co samples, the nickel binder competes with the catalyst, and it becomes difficult to analyze the electrochemical impedance data. Whereas, the electrochemical impedance spectroscopy fitting is found to be improved for the Raney Co/Ni mix material working at high overpotentials, where the best fitting is observed with the experimental data set. In the case of Raney Co/Ni mix, the binder does not participate for the HER (as evidenced through EIS) because the Raney Ni is a better catalyst than Raney Co and the Ni binder. FE-SEM/EDS, EIS analysis and the details presented in the next chapter validate the presence of an oxide in the form of NiO and Ni(OH)₂ likely from the nickel binder.

6.6 References


Chapter 7

7 Raney Nickel Deposition from Modified Watts Plating Bath for Hydrogen Generation

7.1 Introduction*

Carbon dioxide (CO₂) is the principal by-product of the current fossil fuel economy and it has negative externalities such as global warming. As an alternative, a carbon neutral economy¹, such as one supported by hydrogen, would produce energy and water. In this respect, hydrogen generation² can be achieved through thermochemical, electrochemical and biochemical processes. Of all these options, water electrolysis is the most promising method for large scale production of hydrogen and can use a variety of energy sources, such as solar, nuclear and geothermal. However, water electrolysis is quite expensive and energy intensive. To increase the viability of water electrolysis for large scale hydrogen production, overpotentials of the electrode reactions need to be decreased, whilst at the same time the cost of material used to produce the electrodes must also be reduced. The use of inexpensive base metals for the production of electrodes has been widely investigated³.

Water electrolysis consists of two reactions happening simultaneously; hydrogen and oxygen evolution reactions (i.e. HER and OER). Conventional electrode materials for the HER and OER are expensive as they belong to the platinum group, as opposed to nickel based electrodes, which are less costly. The prerequisite

*This chapter is in preparation for publication in a Journal, (2015).
properties of an electrode for water electrolysis include large active surface area, low overpotential and cost⁴. One example of a low cost electrode, is the use of nickel alloys in the production of cathodes. Previous studies of these cathodes have shown their effectiveness in generating HER in alkaline electrolytes³e, 3f, 3h-n, ⁵. Nickel by itself is not highly catalytic toward the HER; however the catalytic properties of the cathode can be improved by the introduction of Raney nickel particles³i, which are a mixture of nickel and a leachable metal, such as aluminium or zinc, to increase the roughness factor or surface area. A conventional method to prepare Raney nickel based electrodes is by electrodeposition. Raney Ni particles coat a substrate by intrusion during nickel electrodeposition, often using a Watts nickel bath.

In this chapter, modifying the conditions of the electrodeposition to change the roughness factor and oxygen content is reported and discussed in detail. To reduce costs, expensive reagents used in the Watts plating solution have been substituted by less costly ones; NiCl₂·6H₂O was substituted with NaCl, other modifications to the Watts bath have been done in other works⁴a, ⁵-⁶. This is done in commercial nickel plating stations as described by Dennis³a as it lowers the nickel finishing cost. In commercial nickel plating, the upper concentration range for nickel sulphate and sodium chloride are 400 and 40 g l⁻¹, respectively. We use these commercial specifications, however the concentration of NaCl is studied at higher values as it is believed that Cl⁻ ions suppress the formation of oxides during electrodeposition⁴b.

Chloride ions are believed to minimize oxidation of Raney Ni particles in solution. Oda⁴b concluded that solutions containing no less than 30 gCl⁻l⁻¹ (NiCl₂·6H₂O as source) should be used, as it clears the passive layer formed on the
surface of the electrode and lowers oxygen content on Raney nickel particles during electrodeposition. The presence of Cl⁻ ions from NaCl, as opposed to Oda’s results, achieves low oxygen content at a lower concentration. This study will investigate the effectiveness of the modified Watts bath for the deposition of Raney nickel and whether this method is competitive to the conventional Watts solution. The validation of this modified finishing process has been evaluated by overpotential curves which have been explained in terms of the presence of passivating species as oxides.

### 7.2 Theory

The section 6.2 in the previous chapter shows the mechanism steps for the HER in alkaline medium. Three steps are universally accepted and shown by Eqs. 6-1 to 6-3. Lasia⁴c analytically derives the electrochemical impedance for one adsorbed specie reaction on porous surfaces. This model is applied for the study of the HER impedance on Raney nickel. The most common equivalent circuits for one adsorbed specie reaction are shown in Fig. 2-9 (in chapter 2) as 1CPE and 2CPE, and are statistically identical. The 1CPE circuit is a modification of the Randles circuit, a mathematical description of this model is done by Lasia⁴c. The 2CPE model is often used³e-n.⁷ as it includes the \( CPE_1 \) and \( R_1 \) elements to represent coating characteristics. For example, in some circumstances \( CPE_1 \) and \( R_1 \) are used to represent the impedance of an oxide coating and for this case their magnitudes are independent of overpotential (\( \eta \)) as they represent the electric capacity and resistance of the coating and they appear in the high frequency region of the impedance.
In our current work, which investigates porous surfaces, $CPE_1$ and $R_1$ represent the porosity in terms of internal mass diffusion of the Raney Ni coating. These values do not necessarily have to be constant, as the reaction rate increases; solution within pores changes its ionic strength. The electrical resistance of a solution is inversely proportional to ionic strength.

Several publications$^{3b, 3i, 3m, 4c, 7-8}$ have calculated $R_{ct}$ and $C_{dl}$ with the 2CPE equivalent circuit. It should be noted that Lasia$^{4c}$ explains that the use of this model can yield biased results as a material containing well defined pores is difficult to synthesize and real porous surfaces contain a distribution of various pores. Lasia$^{7a}$ takes an estimated $C_{dl}$ of 20 $\mu$F cm$^{-2}$ for a smooth metallic electrode to determine a ratio between this value and the experimentally determined $C_{dl}$ from porous electrodes and thus to obtain a roughness factor $r_f$. In this respect, Eq. 2-32 (in chapter 2) determines the average double layer capacitance of porous surfaces for one adsorbed specie reaction.

A discussion about $CPE_1$ and $R_1$ is required to point out the challenges before reaching its conventional interpretation. Lasia mentions the presence of two semicircles during the HER on porous electrodes in alkaline solution; one at high frequency (HF) and another at low frequency (LF)$^{3e-n, 7}$. The HF semicircle is attributed to surface geometry and the LF semicircle to the electrode kinetics. The origin of the HF semicircle was unclear and two different reasons have been presented to explain it$^{3m}$. Since, it has been interpreted as a capacitive loop, related to porosity and thought to remain constant as a function of overpotential, the HF semicircle represents $CPE_1$ and $R_1$. 

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Another contributing factor about the difficulty for the interpretation of the HF semicircle is the time when details were published. Most of the published work about electrochemical impedance of Raney Ni based electrodes have been done during the initial introduction of the EIS technique for electrochemical studies\textsuperscript{3d}. During this initial stage, limitations were found, as for example, artifacts introduced by the reference electrode (RE) at high frequencies\textsuperscript{3d}. It has been attempted to minimize this error by adjusting the RE electrical circuit as shown in Fig. 7-1\textsuperscript{9}. However, there are two RE assemblies which can be used.

Fig. 7-1 shows two different assemblies of a mercury/calomel reference electrode with a Luggin capillary. Fig. 7-1A) shows a Pt wire from the tip of the Luggin to the frit inside the RE and in Fig. 7-1B), the Pt wire extends from the vicinity of the tip of the Luggin to a capacitor, which is connected in parallel to the RE. The assembly A) has been described by Lasia\textsuperscript{3d} as the appropriate RE, however current commercial reference electrodes for EIS are described by the assembly B). The disagreement between RE assemblies probably has generated biased conclusions about EIS on porous surfaces for the HER in previous works. In this respect, Bockris points out that ‘matches of calculated and experimental $Z-\omega$ are seldom exact’ when referring to EIS\textsuperscript{10}, he also says that several things can go wrong matching an equivalent circuit to an interface.
Sadkowski has simulated the error introduced by reference electrodes at high frequencies\(^{11}\). In these simulations the working electrode (WE) shows only one semicircle. Once the reference electrode is introduced then a HF semicircle appears in addition to the LF semicircle found for the WE ‘only’ simulation. Unfortunately, published works do not give details about the RE assembly used during EIS tests\(^{3e-n.7}\). However, one of their authors mentions the assembly A) in Fig. 7-1 to be used for EIS studies.

### 7.3 Materials and methods

#### 7.3.1 Electrode preparation

The plating station consisted of the bath solution, a power supply, nickel and copper sheets as counter and working electrodes having the dimensions of 70 x 50 x 5 mm and 10 x 15 x 1 mm, respectively. One face of the copper sheet was insulated with ferro-lacquer. The solutions used and the preparation conditions for the coatings are shown in Tables 7-1 and 7-2, all the coatings were electrodeposited at \(i = 30\) mA.
cm$^2$. The Raney nickel particles were acquired inactive from Merck having a composition by mass of Ni-Al 50:50 and a maximum particle size of 150 microns. These Ni particles on the coating are activated after electrodeposition in 6.25 M NaOH at 70 °C for 1 h. This makes the coating preparation safe as these particles are pyrophoric upon activation. The samples were dried at 100 °C in air for a period of 1 hour.

### 7.3.2 Linear Voltammetry

A three electrode set up remotely controlled by a BioLogic VSP potentiostat was used. The reference (RE) and counter electrodes (CE) were Ag|AgCl in satd. KCl and a platinised platinum sheet with the dimensions of 10 x 10 x 1 mm, respectively. Tafel plots were determined by linear voltammetry at 25 °C. The samples were made cathodic in 2 M KOH in the HER regime. The sweep rate was 0.1 mV s$^{-1}$ and the sweep range was set arbitrarily from low current densities ($i$) to values in the vicinity of 100 mA cm$^{-2}$. The $IR_{\text{drop}}$ compensation was done by the current interruption method keeping the Luggin at about 5 mm from the electrode. The Ag|AgCl in satd. KCl potential was taken as 197 mV vs. SHE. Finally, the geometric or apparent area of the coatings was used in the determination of current densities.

### 7.3.3 Electrochemical impedance spectroscopy (EIS)

EIS consisted of 3 consecutive scans over the frequency range from 20 kHz to 0.05 Hz, performed one after another at potentials in the HER regime. The ac sinusoidal voltage applied had an amplitude of 5 mV at 25°C. This test was done in sequence after linear voltammetry, no $IR_{\text{drop}}$ compensation was done.
Table 7-1 Electrolytic Solutions Used in the Development of Raney Ni Coatings.

<table>
<thead>
<tr>
<th>Solution ID</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Reagents (Analytical grade)</th>
<th>Concentration g l⁻¹</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Watts Ni</td>
<td>50-60</td>
<td>20</td>
<td>NiSO₄·6H₂O</td>
<td>350</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NiCl₂·6H₂O</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H₃BO₃</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Watts Ni 1/2/3</td>
<td>55</td>
<td>20</td>
<td>NiSO₄·6H₂O</td>
<td>350</td>
<td>3a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NaCl</td>
<td>148/100/40</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H₃BO₃</td>
<td>30</td>
<td></td>
</tr>
</tbody>
</table>

All solutions were vigorously stirred by a magnetic stirrer.

7.3.4 Surface tests

The crystalline structure of the Raney Ni coatings was examined by an EMMA X-ray diffractometer with Cu-Kα radiation. The morphology of the deposits was determined by field emission scanning electron microscopy (FE-SEM) equipped with energy dispersive analysis (EDS) for qualitative elemental analysis using a JEOL instrument, model JSM-7000F.

Table 7-2 Description of the Nickel Coating Conditions.

<table>
<thead>
<tr>
<th>Preparation</th>
<th>Sample ID</th>
<th>Raney Ni concentration (g l⁻¹)</th>
<th>Solution ID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni plate</td>
<td>1</td>
<td>6.25</td>
<td>Acquired</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>12.50</td>
<td>Watts Ni 3 sol.</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>25.00</td>
<td>Watts Ni 2 sol.</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td></td>
<td>Watts Ni 1 sol.</td>
</tr>
</tbody>
</table>

7.4 Results and Discussion

7.4.1 Tafel Plots

Fig. 7-2 shows the Tafel plot for the samples in 2 M KOH solution and Table 7-3 contains their Tafel parameters. The samples are organized into three groups. A first group acting as the control sample, in this group no change in the geometric factor has been done, Ni plate (sample labeled 6) belongs to this group. A second group,
the Raney Ni samples 1 to 3, where all the finishing variables were kept constant but the Raney Ni particle concentration was changed (refer to Table 7-2). A third group, the Raney Ni samples 4 and 5, where the Cl\(^-\) ion concentration (i.e. by adding more NaCl) was changed keeping the other variables constant.

![Experimental HER Tafel Plot for the Samples in 2 M KOH](image)

**Fig. 7-2 Experimental HER Tafel Plot for the Samples in 2 M KOH**

at a Sweep Rate of 0.1 mV s\(^{-1}\).

The overpotential at 100 mA cm\(^{-2}\) has been used to rank the energy efficiency of the samples as shown in Table 7-3. The Raney Ni samples 3 and 4 have the lowest overpotentials ~ 200 mV at 100 mA cm\(^{-2}\). According to Tables 7-1 and 7-2, these two Raney Ni samples were prepared with high Raney Ni particle concentration and low to intermediate concentration of Cl\(^-\) ion. This result is unexpected as low concentration of Cl\(^-\) ion is believed to increase the oxygen content in the surface of the electrodes, lowering energy efficiency. Oxides decrease the electric conductivity of the active layer and this consumes energy, thus lowering energy efficiency. A
sample illustrating a decrease in efficiency (i.e. high $\eta$) related to oxide content is shown here. Sample 5 has a high oxide content as determined by EDS and XPS. In addition, this sample shows an oxide capacitive loop. These results support the hypothesis of passivation due to the formation of oxides during the deposition of the Raney Ni.

Table 7-3 Experimental Electrochemical Parameters for the HER on the Raney Ni Samples in 2 M KOH (per apparent area).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$-b$ (mV dec$^{-1}$) @ $\eta &gt; \eta_{10}$</th>
<th>$-\eta_{100}$ (mV)</th>
<th>$-\log(i_o)^*$ (A cm$^{-2}$)</th>
<th>$R_{ct}^*$ at $\eta_{10}$ ((\Omega) cm$^2$)</th>
<th>$r_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>141</td>
<td>341</td>
<td>3.41</td>
<td>3.95</td>
<td>1304</td>
</tr>
<tr>
<td>2</td>
<td>98</td>
<td>228</td>
<td>3.58</td>
<td>2.52</td>
<td>2202</td>
</tr>
<tr>
<td>3</td>
<td>114</td>
<td>190</td>
<td>3.30</td>
<td>0.97</td>
<td>5371</td>
</tr>
<tr>
<td>4</td>
<td>117</td>
<td>200</td>
<td>3.40</td>
<td>1.38</td>
<td>3063</td>
</tr>
<tr>
<td>5</td>
<td>131</td>
<td>263</td>
<td>3.78</td>
<td>0.89</td>
<td>2100</td>
</tr>
</tbody>
</table>

*: Rounded up values based on their standard deviations.

Overpotentials obtained during this study were compared to reported values in the literature for this type of material. It is reported$^{7b}$ overpotentials at 100 mA cm$^{-2}$ for Ni/Al powder electrodes at 25 °C in 1 M NaOH, ranging from -268 to -521 mV. For smooth nickel, -530 mV of overpotential is published$^{3c}$ at 100 mA cm$^{-2}$. Raney nickel only has overpotentials smaller than -100 mV at 100 mA cm$^{-2}$ when the temperature is 90 °C$^{12-13}$. As is generally accepted, there can be a 20 mV of overpotential decrease for every 10 °C of temperature increase in the alkaline solution. In this respect, the reported overpotentials from this work are competitive to those results published for Raney based electrodes.

Once the overpotential was evaluated, the next variable examined was the Tafel slope. Our work focused on Tafel slopes where the rds belong to kinetic control on
the electrode surface, which indicate adsorption, desorption or a chemical reaction (i.e. Eqs. 6-1 to 6-3). Tafel slopes found in literature$^3g$ range from 121 to 157 mV dec$^{-1}$, and our observed experimental values are from 98 to 141 mV dec$^{-1}$. It was concluded by Cheong et al$^3g$, that the electrochemical HER mechanism in alkaline solutions has the Heyrovsky step as the rds on Raney Ni electrodes. Methods utilized in this article are quite similar to Cheong’s work$^3g$, in terms of electrolyte conditions used (1 M KOH at 25 °C). Results obtained for the Tafel slopes were also comparable, however when data from this study was applied to the simplified Butler-Volmer approach, the Volmer step was rds as opposed to Cheong’s work$^3g$ result for alkaline HER. To theoretically reconcile the Tafel slope, the first step is to propose a reaction mechanism which rds, yields a slope close to that experimentally determined. Further adjustments to a theoretical slope could be achieved by selecting an appropriate isotherm. Another alternative to isotherms is proposing a model which takes into consideration the average pore geometry$^{3b,4c}$.

### 7.4.2 Electrochemical Impedance Spectroscopy

As described in the theory section for EIS data, the 2CPE model$^{14}$ has been selected to determine the impedance of the samples. Figs. 7-3 and 7-4 show the electrochemical impedance of the samples 1 to 5. Table 7-3 shows the variables of interest which were determined by fitting the experimental data. Roughness factors greater than 1000 were found for these samples. Roughness factors in porous Ni/Al electrodes have been reported as high as 5000$^{3l,3l,3m}$, which is comparable to data obtained in our studied samples. In addition, $R_{ct}$ at 10 mA cm$^{-2}$ is used to compare the energy efficiency of the samples (refer to Joule’s effect), as it is more reasonable.
to compare samples under similar current densities than overpotentials. $R_{ct}$ values reported by Hitz$^7b$ are in agreement to those reported in Table 7-3.

The selected overpotential range for EIS studies belongs to the region of current density at about 1 to 10 mA cm$^{-2}$. This region of current density yields stable data. Most impedances show that the fits slightly deviate from the experimental data at the low frequency region, in particular at low overpotentials. It should be noted that at low frequencies, the data collection requires longer periods of time, and the surface coverage could change substantially.

Fig. 7-3 Nyquist impedance (left) and Bode admittance (right) diagrams of the samples 3 and 5, respectively in 2 M KOH solution. Continuous lines represent the fitted curve by the 2CPE model for the sample 3 and a modified 2CPE for the sample 5, experimental data as symbols. The A, B and C areas represent the internal diffusion, charge transfer and oxide impedace domains.
Fig. 7-4 Nyquist impedance (left) and Bode admittance (right) diagrams of the samples 1, 2 and 4, respectively in 2 M KOH solution. Continuous lines represent the fitted curve by the 2CPE model, experimental data as symbols.

The Nyquist impedance and Bode admittance diagrams from the sample 3 in Fig. 7-3 are similar to those commonly found for porous nickel\(^3\), \(^3\)m, \(^7\)b. This is not the case for the sample 5, where from the bode admittance diagram, it can be seen that a third capacitive loop occurs at a log (freq) between 2 and 3. This capacitive loop has been interpreted as the impedance from nickel oxide or hydroxide and fitted by adding an extra capacitive loop to the 2 CPE model. EDS and XPS data supports the presence of significant quantities of oxygen in the coating for the sample 5. The resistance of this third loop was determined to be constant as a function of...
overpotential at about 0.5 Ω cm$^2$. This is the reason why the sample 5, despite of showing a low $R_{ct}$, has a high overpotential as the nickel-oxygen species found in this sample consume energy in the form of an additional resistance.

Fig. 7-3 shows loops corresponding to the impedances from mass transfer, charge transfer and oxide layer. We believe that internal diffusion is a limiting factor on porous surfaces, and this has been found in other fields of chemistry related to porous surfaces. We have interpreted the low frequency (LF) loop to be related to mass transport, and the high frequency (HF) loop to reaction kinetics. In electrochemical impedance analysis, different types of chemical interactions can be related to a certain range of wave frequencies. Particles like hydrogen ions (H$^+$), electrons (e$^-$) have substantial different masses and require different times of application of an external force from an electric field to experience motion.

Heavier particles like hydrogen ions require the application of an external force for longer times and this is expected to happen at lower wave frequencies than in the case of electrons. This is the main reason why mass transfer is assigned to happen at the low frequency region in the Bode admittance plot. The LF loop is related to mass transport and it is controlled by the concentration of electrolyte within the pores which determines $R_1$, and it is found below 0 of the log (freq). Diffusion elements manifest themselves in most cases in frequencies smaller than 10 Hz, which supports the reasoning that the LF loop found on porous surfaces is related to mass transport. In the appendix B, the origin of the mass, kinetic and oxide capacitive loops found by EIS are explained.
Continuing with our reasoning about HF and LF loops, we have considered $R_{ct}$ to be relatively constant (i.e. its magnitude changes little as a function of overpotential). Our previous work about oxygen evolution\cite{30} shows that $R_{ct}$ does not change by orders of magnitude as a function of overpotential and its capacitive loop is found between 0 to 2 of the $\log$ (freq), and we have used these results to support the view that $R_{ct}$ for the HER on porous surfaces, changes smoothly as a function of overpotential. By considering the previous explanation, we have interpreted that the HF loop is related to $R_{ct}$.

The reaction kinetics or charge transfer domain shown in Fig. 7-3 as the B area, has a phase (Y) peak at about 1 of the log (freq) in all the samples, except for sample 1 whose peak is shifted to the right. This is an indication that for the sample 1, the nickel binder is competing with the Raney nickel as this sample was prepared with the smallest concentration of Raney particles at 6.25 g l$^{-1}$. This is in agreement with the overpotential found for the sample 1, which is relatively high. This peak shift has been explained in terms of the M-H reaction intermediate, ‘M’ could be nickel from the binder or Raney particles and these two have different M-H intermediates and impedances. Different impedances shift the location of the peak belonging to charge transfer.

Samples 3 and 4 generated the most favourable overpotentials for the HER and showed relatively low charge transfer resistances as shown in Table 7-3. Samples 3 and 4 were determined to have high roughness factors which explains their overpotential improvement when compared to nickel plate (i.e. sample of control labelled 6). Samples 1, 2 and 5 have higher overpotentials due to an unfavourable
combination of high $R_{ct}$, low $r_t$ and the presence of additional impedance from oxides.

The oxide content determined from FE-SEM/EDS and XPS, it should be noted that samples having about 1% by mass of oxygen showed no third capacitive loop (cf. Table 7-4). Particular attention should be taken for the sample 4 which does not show a third capacitive loop despite of having 3.25% of oxygen. The only sample which was fitted by including an extra capacitive loop was number 5 as it has a considerable amount of oxygen at 11.6%. Assuming a linear behaviour between the oxygen composition and oxide electrical resistance, 1% of oxygen would represent a resistance lower than 0.05 $\Omega$ cm$^2$, which is practically negligible when compared to most $R_{ct}$ values.

### 7.4.3 X-ray Diffraction Spectra

Fig. 7-5 shows the XRD spectra of all the tested samples. Results in Fig. 7-5 were expected as Watts bath electrodeposits nickel. The peaks corresponding to copper are identified which are originated from the substrate. All the samples show the synthetic nickel peaks. No nickel oxide peak was identified by XRD in any of the samples, in particular for the sample 5 which shows high oxygen concentration by EDS and XPS. This makes us believe that the nickel oxide phase is amorphous or it is below the detection limits of the XRD.
7.4.4 SEM Micrographs Associated with Elemental Analysis

Fig. 7-6 shows the FE-SEM micrographs of the Raney Ni samples 3 and 5. These materials show porosity at the micron scale and the porosity distribution is not uniform. These results support the selection of the 2CPE model for EIS data fitting, as this model is for porous surfaces. SEM/EDS results in Table 7-4 shows the oxygen content of the samples, where the samples 1 to 3 show about 1% oxygen (i.e. low oxygen content) and samples 4 and 5 show higher oxygen contents (i.e. high oxygen content). Sample 3 was of particular interest as measurements showed low oxygen content, as well as the most favorable overpotential for the HER when compared to the other samples. This result supports the hypothesis of the effect of oxygen content on the HER in Raney Ni electrodes. Previous publications indicated the problems associated with the presence of oxygen in the form of nickel oxide, as it passivates the Raney nickel material thus increasing its overpotential for the HER. Samples showing high oxygen content, contained in their plating solution...
high to intermediate concentrations of NaCl. The greater the concentration of NaCl, the greater the oxygen content as found in samples 4 and 5.

![Fig. 7-6 FE-SEM Micrographs of the Raney Ni Samples 3 and 5, labelled a and b, respectively.](image)

Table 7-4 Oxygen Elemental Dispersive Analysis of the Raney Ni Electrodes.

<table>
<thead>
<tr>
<th>Concentration by mass (%)</th>
<th>Raney Ni sample ID</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>1     2</td>
</tr>
<tr>
<td></td>
<td>1.14  1.08</td>
</tr>
</tbody>
</table>

7.4.5 X-ray Photoelectron Spectroscopy

Fig. 7-7 shows the XPS spectra of the samples 3 and 5. This result shows the nature of the oxygen observed through FE-SEM/EDS analyses. Only the XPS spectra from the samples 3 and 5 are shown as they have low and high oxygen content. The sodium spectrum in Fig. 7-7(a) has been included as it has been detected in most XPS plots. Fig. 7-7(a) shows that the sample 5 has a substantial higher concentration of sodium and this is supported by additional sodium peaks shown in Fig. 7-7(c and d). By combining the information from Figs. 7-7(b) and 7-
7(c), it is determined that the oxygen content found in the samples is related to two types of oxygen (i.e. metal oxide and metal hydroxide). The sample 5 shows no evidence for metal oxide but its metal hydroxide peak has higher intensity than that from the sample 3. Metal hydroxides are nonconductive and this would explain the additional capacitive loop found in the sample 5 by EIS plots. In this respect, increasing the NaCl concentration in the modified Watts bath, appears to suppress the formation of metal oxide but it increases the formation of metal hydroxide as the sample 5 shows no peak where metal the oxide is expected (Fig. 7-7(c)). Nickel hydroxide is worse than nickel oxide in terms of oxide impedance, the former is less electric conductive.

Figure 7-7 XPS spectra of the samples 3 and 5. Na(1s), Ni(2p), O(1s) and Al(2p) labelled as (a), (b), (c) and (d) respectively. Note that (c) also shows the Na Auger peak as Na KLL.
Considering the O(1s) peak parameters from K. Shimizu et al.\textsuperscript{15}; O\textsuperscript{2−}, OH\textsuperscript{−} and H\textsubscript{2}O peaks are found at 530.8-531.2, 531.9-532.3 and 534.4 eV, respectively. This has led us to consider that the main peak found in Fig. 7-7(c) to belong to Ni(OH)\textsubscript{2} and the other peak to NiO. The water content of the samples 3 and 5 is negligible. To support the reasoning about NiO and Ni(OH)\textsubscript{2}, Fig. 7-7(b) includes the Ni(2p\textsubscript{3/2}) spectra from the samples 3 and 5. Ni peak parameters from Grosvenor\textsuperscript{16} were taken; Ni\textsuperscript{0} main peak is found at 852.6 eV and Ni\textsuperscript{2+} intensity increases in a multi-peak envelope near 856.1 eV. The Ni(2p\textsubscript{3/2}) spectrum from the sample 3 gives a clear indication of the presence of nickel-oxygen species in addition to pure nickel. The origin of oxygen species determined by XPS in the Raney coating has been explained in the 6.4.4 section in the previous chapter.

One solution for the high Ni(OH)\textsubscript{2} content found in sample 5 would be heat treatment. How effective heat treatment would be in removing hydroxyl is not entirely clear. It has been determined that nickel hydroxide during heat treatment losses hydroxyl in the form of water leaving nickel oxide as the final product\textsuperscript{17}, nickel oxide is also nonconductive. Zech\textsuperscript{6b} shows other options to decrease the oxygen content during electrodeposition in Watts bath, such as changing reagents and their concentrations. However, when the oxide impedance is negligible, as in the case of the Watts bath number 3 (cf Table 1), whose EIS data does not show an oxide impedance. This result validates the use of the Watts bath number 3 as it achieved low oxygen content, and yield good results (i.e. results from sample 3).
7.5 Conclusions

Raney nickels are characterized by having high roughness factors, which increase the surface area of the electrodeposited electrode and the availability for the hydrogen evolution reaction to occur. However, a high roughness factor does not necessarily indicate high catalytic activity. Oxygen content has a direct influence on the overpotentials for the HER of Raney nickel electrodes. This effect was found in samples 5 in particular, which shows high roughness factors, but low electroactivity due to its high oxygen content. These conclusions are based on the polarization plots obtained, which are supported by impedance spectroscopy. The XPS and FE-SEM/EDS results aid the proposed analysis as they determined oxides in the coatings. Passivation of Raney Ni particles occur during the plating process by the formation of nickel oxides. The presence of nickel oxides was indirectly identified by EIS in addition to XPS and EDS.

7.6 References


8 General Conclusions and Recommendations

This thesis describes the results of an investigation of the electrochemical properties of new electrodes for efficient water electrolysis. The emphasis of the work has been to improve the energy efficiency of the electrodes through altering their physico-chemical properties. To be specific, one of the objectives has been to determine while altering the geometric and electronic factors whether the catalytic activity of materials can be enhanced and to identify its mechanism. The overall focus of this thesis is to map viable lower cost substitutes for expensive platinum group as catalysts. The main conclusions of this study and recommendations for future work are outlined in this chapter.

8.1 Conclusions

Electrolytic manganese dioxide (γ – MnO$_2$) is a well-researched area and has found wide applications in the field of electrochemistry. Whereas, in this work, we have used the modified version of this material for water electrolysis. The electronic factor has been modified by adding dopants which would generate intermediate bond strength with the reaction intermediate. We found that the Mo/Co doping combination in EMD is competitive in terms of overpotential for acid oxygen evolution reaction (OER). This bimetallic addition resulted in 305 mV of overpotential ($\eta$) which is competitive to that of commercially available DSA®
material which exhibits 341 mV at the same current density. The obtained results are supported by linear voltammetry and electrochemical impedance spectroscopy (EIS) analyses. The charge transfer resistance by EIS from the best modified EMD is 0.290 Ω cm² at η₁₀. this value is competitive to that of commercial DSA®. This illustrates, modifying the EMD can positively influence its electrochemical properties toward the OER. The challenge lies on identifying correct element pair combinations, although our approach was more empirical than systematic. An extensive computational and theoretical background may help in revealing the full picture.

The work related to porous Raney surface type such as those from nickel and cobalt, enhances the available area for the hydrogen evolution reaction (HER) to occur which increases its energy efficiency. The modified Watts bath by substituting nickel chloride with sodium chloride shows good results. The nickel binder from a modified Watts bath brings two benefits. The cost of the bath is decreased and the energy efficiency of the material toward the HER is competitive when compared to other materials of the same category (i.e. porous materials). Porous materials based on nickel and cobalt, have been reported to be synthesized by other techniques, however we selected electrodeposition for our studies. This is probably the simplest technique of all, for catalyst preparation. The crucial variable for Watts baths is the deposition of oxides which exhibit high impedance that decreases the energy efficiency of materials.

Porous nickel is the best option for the HER, as opposed to porous cobalt. Porous cobalt for the HER is not a good option, despite of showing good catalytic properties for the HER in Volcano plots. Other secondary new knowledge obtained by working
with porous surfaces is related to the source of inefficiencies in the form of additional electrical resistance that does not actively participate in the HER. We were able to identify the source of this additional resistance in the nickel binder from hydroxides or oxides.

8.2 Recommendations for Future Research

The work described in this thesis suggests that EMD in the presence of dopants and porous Raney materials should be suitable candidates for efficient water electrolysis. It is, however, important to note that only selected dopants were investigated in this work. Before commercial applications can be considered, further extensive work on computational modeling is needed to assess and optimize the concentration of dopants. There are always directions to improve this technology and to make it less expensive and more efficient. Some recommendations for further work, not in any particular order, are listed below:

- Carry out further research on the influence of various dopants in EMD to improve the catalytic activity. Some potential dopant candidates are those combinations from each side of Volcano plots (refer to chapter 2).
- To develop models for pore geometry that can assist in impedance fitting from the obtained results.
- Investigate catalyst carriers and find a suitable binder that would place the electrode material on a surface with high roughness factor.
- Examine other porous catalyst carriers and its consequent effect on the electronic and geometric factor and their suitability in water electrolysis.
Appendix A

This appendix presents some calculation examples.

1. Activity coefficients of hydrogen and hydroxide ions in aqueous solution.

To determine the equilibrium or cell potential of water electrolysis, it is needed the activity coefficients of the ions involved. In this example, acid electrolysis at 2 M H₂SO₄ and KOH are analyzed, for which the following assumptions are made:

a) The laboratory temperature is constant at 25 °C.

b) The mean salt method determines the individual ion activity accurately.

c) The MacInnes assumption, where \( \gamma_{\pm KCl} = \gamma_{K^+} = \gamma_{Cl^-} \) is taken [1].

Geometric mean ionic molal activity coefficient of the solute (adim.):

\[
\gamma_\pm = (\gamma_+^{\nu_+} \times \gamma_-^{\nu_-}) ^ {1/(\nu_+ + \nu_-)} \quad \text{A- 1}
\]

where:

\( \gamma_+, \gamma_- \): ionic individual coefficients (adim.).

\( \nu = \nu_+ + \nu_- \): stoichiometric coefficients of electrolyte dissociation into \( \nu_+ \) cations and \( \nu_- \) anions (adim.).

The hydrogen ion activity coefficient is determined from the stoichiometric coefficients of sulphuric acid dissociation followed by the Eq. A-1 as shown

Sulphuric acid disassociation reaction:

\[
H_2SO_4 \rightarrow H^+ + HSO_4^-
\]
Therefore:

\[
γ_{±H_2SO_4} = \sqrt{γ_{H^+} × γ_{HSO_4^-}}
\]

The individual activity coefficient of hydrogen ions is

\[
γ_{H^+} = \frac{γ_{±H_2SO_4}^2}{γ_{±HSO_4^-}}
\]  

A-2

To make this calculation, a double bridge is needed to determine the activity coefficient of bisulphate. Therefore the disassociation reaction of potassium bisulphate is

\[
KHSO_4 → K^+ + HSO_4^- 
\]

For this reaction, the mean activity coefficients becomes

\[
γ_{±KHSO_4} = \sqrt{γ_{K^+} × γ_{HSO_4^-}}
\]

Rearranging with the MacInnes assumption

\[
γ_{HSO_4^-} = \frac{γ_{±KHSO_4}^2}{γ_{±KCl}}
\]  

A-3

Combining the activity coefficients from sulphuric acid and potassium bisulphate and taking the MacInnes assumption, the individual activity coefficient for hydrogen ions is determined by Eqs. A-2 and A-3. Mean activity data from sources [2,3] is given in molal concentrations, this is fixed by a conversion factor from molar to molal. This requires another assumption, the density of water is rounded to 1000 kg m\(^{-3}\), therefore molar and molal concentrations are equivalent.
At 25 °C and 2 M concentrations for KCl, H₂SO₄ and KHSO₄, the mean activity coefficients are [2,3]; 0.574, 0.151 and 0.089, respectively. Evaluating Eqs. A-2 and A-3, the hydrogen ion activity coefficient is 1.65 as shown.

\[
\gamma_{\text{HSO}_4^-} = \frac{0.089^2}{0.574} = 0.0138
\]

and

\[
\gamma_{\text{H}^+} = \frac{0.151^2}{0.0138} = 1.65
\]

For the case of the hydroxide ion activity coefficient determination, similar procedure as that from the sulphuric acid is done as follows:

Potassium hydroxide disassociation reaction:

\[
\text{KOH} \rightarrow \text{K}^+ + \text{OH}^-
\]

Thus, \( \gamma_{\pm\text{KOH}} = \sqrt{\gamma_{\text{K}^+} \times \gamma_{\text{OH}^-}} \) is derived and rearranging it (including the MacInnes assumption), the individual activity coefficient of hydroxide ions is

\[
\gamma_{\text{OH}^-} = \frac{\gamma_{\pm\text{KOH}}^2}{\gamma_{\pm\text{KCl}}} \quad \text{A- 4}
\]

At 25 °C and 2 M concentrations for KCl, KOH, the mean activity coefficients are [2,3]; 0.574 and 0.863, respectively. Evaluating the Eq. A-4, the hydroxide ion activity coefficient is 1.30 as shown (rounded up).

\[
\gamma_{\text{OH}^-} = \frac{0.863^2}{0.574} = 1.30
\]
2. Equilibrium potential of water electrolysis

To determine the equilibrium or cell potential of water electrolysis, first the half cell potentials have to be determined. On this example, acid electrolysis at 2 M H₂SO₄ is analyzed. The following assumptions are made, in addition to those from the example 1:

d) The partial pressure of hydrogen and oxygen equals 101,325 Pa (1 atm), the reference condition is 1 atm therefore the activity of these gases is unity.
e) The individual activity coefficient of hydrogen ions does correct the concentration to activity.

To determine the non-standard cell potential of water electrolysis, the HER and OER equations and their standard potentials are required as the first step. Then, the Nernst equation is used to adjust the standard potential to the conditions of the reaction, during this step the activity coefficient of either hydrogen or hydroxide ions is required, depending on the solution pH. These steps are described as follows

Half cell potential at standard conditions:

**HER**

\[ 2H^+ + 2e^- \rightarrow H_2(g) \quad E_{\text{red}}^o = 0.00 \text{ V} \quad \text{A-5} \]

**OER:**

\[ 2H_2O \rightarrow O_2(g) + 4H^+ + 4e^- \quad E_{\text{red}}^o = +1.229 \text{ V} \quad \text{A-6} \]
Water Electrolysis:

\[ 2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2(g) \quad E_{\text{cell}}^o = -1.229 \text{ V} \quad \text{A- 7} \]

The reaction is non-spontaneous as its Gibbs energy is positive as calculated from Eq. 2-3 (section 2.1):

\[ \Delta G^o = -2 \times 96485.34 \text{ C mol}^{-1} \times (-1.229 \text{ V}) = 237.16 \text{ kJ mol}^{-1} \]

\[ \Delta G^o = 237.16 \text{ kJ mol}^{-1} \]

The reaction is not at standard conditions of concentration and temperature, the non-standard cell potential has to be calculated from Eq. 2-2 (section 2.1).

Consider:

\[
\frac{RT}{F} = \frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times (25 ^\circ \text{C} \times \frac{1\text{ K}}{1\text{ ^\circ\text{C}} + 273.15 \text{ K})}}{96,485.34 \text{ C mol}^{-1}} = 0.05917 \text{ V}
\]

and the hydrogen ion activity:

\[ a_{H^+} = \gamma_{H^+} \times \frac{[H^+]_{\text{electrolyte}}}{[H^+]_{\text{reference state}}} = 1.65 \times \frac{2 \text{ M}}{1 \text{ M}} = 3.3 \text{ Adim} \]

The HER cell potential is:

\[
E_{\text{red}} = 0.00 \text{ V} - \frac{0.05917 \text{ V}}{2} \times \log \left( \frac{a_{\text{H}_2(\text{g})}}{a_{H^+}^2} \right) = -0.02958 \text{ V} \times \log \left( \frac{1}{3.3^2} \right)
\]

\[ = 0.03067 \text{ V} \]

\[ E_{\text{red}} = 0.03067 \text{ V} \times \frac{1000 \text{ mV}}{1 \text{ V}} = 30.67 \text{ mV} \]

\[ E_{\text{red}} = 30.67 \text{ mV} \]
The OER cell potential is:

\[ E_{\text{red}} = +1.229 \text{ V} - \frac{0.05917 \text{ V}}{4} \cdot \log \left( \frac{1}{a_{H^+} a_{O_2(g)}} \right) \]

\[ E_{\text{red}} = +1.229 \text{ V} - 0.01479 \text{ V} \cdot \log \left( \frac{1}{3.3^4} \right) \]

\[ E_{\text{red}} = +1.25967 \text{ V} \cdot \frac{1000 \text{ mV}}{1 \text{ V}} = +1259.67 \text{ mV} \]

\[ E_{\text{red}} = +1259.67 \text{ mV} \]

\[ E_{\text{cell}} = 30.67 - 1259.67 \text{ mV} = -1229 \text{ mV} \]

\[ E_{\text{cell}} = -1229 \text{ mV} \]

3. Enthalpy of water disassociation

Water Electrolysis:

\[ 2\text{H}_2\text{O(l)} \rightarrow 2\text{H}_2(g) + \text{O}_2(g) \]

<table>
<thead>
<tr>
<th>Table A-1. Standard enthalpies of formation.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Standard enthalpies of formation (( \Delta H_f^o \text{ kJ mol}^{-1} ))</strong></td>
</tr>
<tr>
<td>---------------------------------------------</td>
</tr>
<tr>
<td><strong>-285.84</strong></td>
</tr>
</tbody>
</table>

From Hess’s law:

\[ \Delta H_d^o = \Delta H_{products}^o - \Delta H_{reactants}^o \]

\[ \Delta H_d^o = (2 \cdot 0.0 \text{ kJ mol}^{-1} + 0.0 \text{ kJ mol}^{-1}) - 2 \cdot (-285.84 \text{ kJ mol}^{-1}) \]
Appendix A A-200

Standard enthalpy of water disassociation:

\[ \Delta H_d^\circ = 571.68 \text{ kJ mol}^{-1} \]

Every mol of liquid water at standard conditions requires a minimum of 571.68/2 kJ mol\(^{-1}\) of energy to split it (i.e. 285.84 kJ mol\(^{-1}\)).

4. Gas production

During water electrolysis, gases evolve. Hydrogen and oxygen evolve as a function of electrical current and charge. For this calculation, Eqs. A-10 and A-11 are used. This example shows how to estimate the volume of hydrogen. An experiment is run for 1 hour. The conditions are P=1 atm, T=25 °C and I=100 mA. The volume of hydrogen produced is estimated from an energy balance and applying the ideal gas law.

Considering the following equations:

Electrical charge:

\[ Q = It \quad \text{A- 10} \]

where:

\( Q \): electrical charge (C).

\( I \): electrical current (A).

\( t \): time (s).

Ideal gas law:

\[ PV = nRT \quad \text{A- 11} \]
where:

\( P \): total gas pressure (Pa).

\( V \): total volume \((\text{m}^3)\).

\( n \): amount of substance (mol).

\( R \): Universal gas constant \((8.314 \text{ J mol}^{-1} \text{ K}^{-1})\).

\( T \): Absolute temperature (K).

Energy balance,

\[
Q = \left(100 \text{ mA} \times \frac{1 \text{ A}}{1000 \text{ mA}} \right) \times (1 \text{ hr} \times \left(\frac{60 \text{ min}}{1 \text{ hr}} \times \frac{60 \text{ s}}{1 \text{ min}}\right) = 360 \text{ C}
\]

\( Q = 360 \text{ C} \)

The moles of electrons are:

\[
\frac{360 \text{ C}}{96485.34 \text{ C mol}^{-1}} = 3.7311 \times 10^{-3} \text{ mol}
\]

Every mol of gaseous hydrogen requires 2 moles of electrons, therefore the total mol of hydrogen is:

\[
n_{H_2} = 3.7311 \times 10^{-3} \text{ mol e}^- \times \frac{1 \text{ mol H}_2}{2 \text{ mol e}^-} = 1.8656 \times 10^{-3} \text{ mol}
\]

\( n_{H_2} = 1.8656 \times 10^{-3} \text{ mol} \)

Volume of produced hydrogen is:
\[ V = \frac{1.8656 \times 10^{-3} \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times (25^\circ \text{C} \times \frac{1 \text{ K}}{1^\circ \text{C}} + 273.15 \text{ K})}{1 \text{ atm} \times \frac{101325 \text{ Pa}}{1 \text{ atm}}} \]

\[ V = 4.564 \times 10^{-5} \text{ m}^3 \]

\[ V = 4.564 \times 10^{-5} \text{ m}^3 \times \frac{1 \times 10^6 \text{ ml}}{1 \text{ m}^3} = 45.64 \text{ ml} \]

\[ V = 45.64 \text{ ml} \]

5. Gas solubility:

The solubility of hydrogen in water at the same conditions as described on the gas production calculations (example 4) is determined by the Henry’s Law:

\[ P = k_H c \]

where:

c: gas solubility (mol l\(^{-1}\)).

k: constant of solubility (l atm mol\(^{-1}\)).

P: Partial gas pressure above the solution (atm).

The solubility of hydrogen in water is then:

\[ c_{H_2} = \frac{1 \text{ atm}}{1282.05 \text{ l atm mol}^{-1}} = 78 \times 10^{-4} \text{ M} \]

\[ c_{H_2} = 78 \times 10^{-4} \text{ M} \]

The same calculation for oxygen yields:
Appendix A A-203

\[ c_{O_2} = \frac{1 \text{ atm}}{769.21 \text{ atm mol}^{-1}} = 13 \times 10^{-3} \text{ M} \]

\[ c_{O_2} = 13 \times 10^{-3} \text{ M} \]

This is the maximum gas content the water can take when the partial gas pressure of gas equals 1 atm.

6. Wet gas composition

The experiment described on the gas production calculation (i.e. example 4) does not mention that the gas produced has a portion of water vapor; the maximum content of vapor in this gas phase is determined by the Antoine equation:

\[
\log(P_w) = A - \frac{B}{C+T}
\]

where:

T: temperature (°C).

\( P_w \): partial water vapor pressure (mmHg).

A, B and C: empirical component-specific constants (for water A=8.07131; B=1730.63; C=233.426).

However, the gas in the cathode chamber is a mixture of two gases, water vapor and hydrogen. Eq. A-14 is used to determine the partial pressure of hydrogen.

Dalton’s law:

\[ P = \sum_{i=1}^{n} P_i \]

where:
P: total pressure of the system (Pa).

$P_i$: partial pressure of gas number i (Pa).

The maximum water partial pressure for the gas production experiment is (Eq. A-13):

$$P_w = 10^{\frac{0.07131}{233.426+25} - \frac{1730.63}{233.426+25}} = 10^{1.3745} = 23.69 \text{ mmHg}$$

$$P_w = 23.69 \text{ mmHg} \times \frac{101325 \text{ Pa}}{760 \text{ mmHg}} = 3157.93 \text{ Pa}$$

$$P_w = 3157.93 \text{ Pa}$$

The partial hydrogen pressure is (Eq. A-14):

$$101325 \text{ Pa} = P_w + P_{H_2} = 3157.93 \text{ Pa} + P_{H_2}$$

$$P_{H_2} = 98167.06 \text{ Pa}$$

7. Tafel slope

With a Butler-Volmer approach is possible to estimate the Tafel slope, if the reaction mechanism is known. In the case of HER in acid with the same conditions as the second example and assuming Tafel as the rds the HER mechanism is:

Table A-2. HER mechanism steps in acid solution.

<table>
<thead>
<tr>
<th>Step description</th>
<th>Steps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge transfer step preceding the rds.</td>
<td>$M + H_3O^+ + e^- \rightleftharpoons M - H + H_2O$</td>
</tr>
<tr>
<td>Chemical step (rds).</td>
<td>$M - H + M - H \rightleftharpoons H_2 + 2M$</td>
</tr>
</tbody>
</table>
According to Eqs. 2-23 to 2-28 (section 2.5.1.1), there are two electrons being transferred before the rds, the rds preceding step has to happen twice for every diatomic hydrogen. The rds is a chemical step as no electrons are involved. Finally, the Tafel slope is calculated by the Eqs. A-15 and A-16 and shown in Table 3:

\[
\frac{d\eta}{d\log i} = \frac{59.16 \text{ mV}}{\alpha} \quad \text{A- 15}
\]

\[
\tilde{\alpha} = \frac{\gamma}{\nu} + r\beta \quad \text{A- 16}
\]

where:

\( \beta \): Symmetry factor, assumed as 0.5 (Adim.).

Table A-3. Forward transfer coefficients (cathodic) \( \tilde{\alpha} \) HER mechanisms (assuming \( \beta=0.5 \)) where \( \gamma, \tilde{\gamma}, r, \nu \) and \( n \) are known.

<table>
<thead>
<tr>
<th>Rate determining step (rds)</th>
<th>Electrons transferred preceding the rds (( \gamma ))</th>
<th>Electrons transferred postceding the rds (( \tilde{\gamma} ))</th>
<th>rds reaction type (( r ))</th>
<th>Stoichiometric number (( \nu ))</th>
<th>Number of electrons transferred (( n ))</th>
<th>Cathodic transfer coefficient (( \tilde{\alpha} ))</th>
<th>Estimated Tafel slope mV/dec (( d\eta/d\log i ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tafel</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>2.0</td>
<td>29.5</td>
</tr>
</tbody>
</table>

8. Overpotential

The overpotential determines how far from the equilibrium potential, the reaction is. This example shows the case where the half cell reaction is the HER on nickel and the conditions are the same as those from the example number 2. From a three electrode set up the following data is given.

Data:

Current density = 100 mA cm\(^{-2}\).
Reference-Working electrodes potential difference = -689.40 mV (this value is negative for the cathode).

Reference electrode Ag/AgCl potential = 197.00 mV (at 25 °C).

Calculated HER equilibrium potential vs. SHE = 30.67 mV.

The Reference-Working electrodes potential difference is:

$$\Delta E_{RW} = E_W - E_{RE}$$  \hspace{1cm} \text{A- 17}$$

where:

$E_W$: potential of the working electrode (mV).

$E_{RE}$: potential of the reference electrode (mV) (adjusted to the electrolyte solution temperature).

Rewriting the Eq. A-17 for the cathode as the working electrode, one has

$$\Delta E_{RC} = E_C - E_{RE}$$

where:

$E_C$: potential of the working cathode (mV).

The overpotential is:

$$\eta = E_C - E_e$$  \hspace{1cm} \text{A- 18}$$

Therefore,

$$E_C = \Delta E_{RC} + E_R = -689.40 \text{ mV} + 197.00 \text{ mV} = -492.40 \text{ mV}$$

$$E_C = -492.40 \text{ mV}$$
The overpotential is:

\[ \eta = E_C - E_e = -492.40 \text{ mV} - 30.67 \text{ mV} = -523.07 \text{ mV} \]

\[ \eta = -523.07 \text{ mV} \]

It can be seen that the overpotential is negative for the cathode. The overpotential is always negative for cathodes and positive for anodes. The Tafel plot always shows the I-E curve in the first quadrant, this requires a change of the cathodic overpotential sign.

9. Gas volume by water displacement

Hydrogen and oxygen from water electrolysis evolve and their volume is measured by water displacement on a constant internal diameter cylinder. The gas displaces the water level and the difference gives its volume. The volume measurement system consists of a vertical column of liquid in a tube that has ends which are exposed to different pressures, one end is closed and the other is at atmospheric pressure.

The gas collected on the closed end of the column of liquid is at a higher pressure than the other end, however due to the size of the samples taken and the capillary effect of the experimental set up, the difference of pressure turns out to be negligible. Therefore, the samples taken are assumed to be at atmospheric pressure.

Data:

Difference of liquid meniscus height: 62.0 mm.
Internal cylinder diameter: 4.85 mm.

Volume of a cylinder:

$$V = \pi r^2 h$$  \hspace{1cm} \text{A-19}

Volume of gas produced is:

$$V = \pi \left( \frac{4.85 \text{ mm}}{2} \right)^2 \times 62.0 \text{ mm} = 1145.42 \text{ mm}^3 \times \frac{0.001 \text{ ml}}{1 \text{ mm}^3} = 1.145 \text{ ml}$$

$$V = 1.145 \text{ ml}$$

The moles of gas are calculated with the ideal gas law, as done in the gas production example.

**References**


Appendix B

This appendix contains miscellaneous information.

1. List of isotherms

<table>
<thead>
<tr>
<th>Isotherm Name</th>
<th>Equation</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$\beta a = \frac{\theta}{1 - \theta}$</td>
<td>Considers the basic step of the adsorption reaction</td>
</tr>
<tr>
<td>Frumkin</td>
<td>$\beta a = \frac{\theta}{1 - \theta} e^{-2a\theta}$</td>
<td>Considers lateral interactions</td>
</tr>
<tr>
<td>Virial</td>
<td>$\beta a = \Gamma e^{2Bz\tau}$</td>
<td>Considers heterogeneity</td>
</tr>
<tr>
<td>Temkin</td>
<td>$\beta a = e^{f\theta}$</td>
<td>Considers heterogeneity</td>
</tr>
<tr>
<td>Conway and Angerstein-Kozlowska</td>
<td>$\beta a = \frac{\theta}{1 - \theta} \exp(K\theta z - \frac{gPV}{RT})$</td>
<td>Considers partial transfer of charge between adsorbed molecule and the substrate</td>
</tr>
<tr>
<td>Parsons</td>
<td>$\beta a = f(\Gamma) \exp\left(\frac{e_0\Delta\phi}{K_q} \left[ g_x - \lambda(1 - g) \right] \right)$ $\times \exp\left(\frac{e_0 q'}{K_{q'}} \left[ zh - \lambda(1 - h) \right] \right)$</td>
<td></td>
</tr>
<tr>
<td>Habib and Bockris</td>
<td>$\beta a = \frac{\theta}{e^{p-1}(1 - \theta)^p}$</td>
<td>This is a more complex Flory-Huggins type isotherm</td>
</tr>
<tr>
<td></td>
<td>$\times \exp\left(\alpha_2 \theta^{1/2} \sum_{n=1}^{\infty} \left[ 1 - (1 + \frac{h'\theta}{n^2})^{-1/2} \right] \right)$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\times \exp\left(\alpha_3 \theta^3 \sum_{n=1}^{\infty} \frac{1}{n^5} \left[ 1 + (1 + \frac{h'\theta}{n^2})^3 \right] \right)$</td>
<td></td>
</tr>
</tbody>
</table>
2. Impedance equation example

Consider the following mechanism where B, P are chemical species and X an adsorbate specie.

\[ B \xrightarrow{k_1} X + e^- \]

\[ X \xrightarrow{k_2} P + e^- \]

**Table B-2. Impedance for Heterogeneous Reactions**²

<table>
<thead>
<tr>
<th>Method Name</th>
<th>Equation</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epelboin</td>
<td>[ Z(\omega) = \frac{1}{F A} \left( k_1 c_B + k_2 \right) ] [ b_1 + b_2 + \frac{(b_1-b_2)(-k_1 c_B + k_2)}{\omega\beta + k_1 c_B + k_2} ]</td>
<td>Based on Tafel law and Langmuir isotherm</td>
</tr>
<tr>
<td>Frumkin and Armstrong</td>
<td>[ Y(\omega) = \frac{1}{R_{ct}} \left[ \left( \frac{\partial v_1}{\partial \Gamma} \right)<em>E + \left( \frac{\partial v_2}{\partial \Gamma} \right)<em>E - \left( \frac{\partial v_1}{\partial E} \right)</em>\Gamma - \left( \frac{\partial v_2}{\partial E} \right)</em>\Gamma \right] ]</td>
<td>No assumptions are required</td>
</tr>
</tbody>
</table>

In both equations the diffusion effect has been neglected.

where:
- \( A \): electrode area
- \( b_i \): Tafel’s slope
- \( c_i \): concentration of species \( i \)
- \( E \): potential
- \( F \): Faraday’s constant
- \( j \): imaginary operator
- \( k_i \): rate constant of the forward reaction
- \( R_{ct} \): charge transfer resistance
- \( v_i \): reaction rate
- \( Y(\omega) \): admittance
- \( Z(\omega) \): impedance
- \( \beta_i \): maximum surface concentration of species \( i \)
- \( \Gamma_i \): surface concentration of species \( i \)
- \( \tau \): time constant of the admittance
3. Example of a Tafel analysis by different isotherms

Consider the following hydrogen evolution Tafel analysis where the rds is the second step as shown below

\[ M + H_2O + e^- \xrightarrow{k_1} MH + OH^- \]  

\[ MH + MH \xrightarrow{k_2} H_2 + 2M \]

In this worked out example it is shown the Tafel slope derivation from two different isotherms, Langmuir and Frumkin-Temkin. This example is for simple cases, this might not be the situation for other cases which are laborious. It is out of the scope of this research the study of more complex situations. This example is to show the difficulty involved when performing a Tafel slope analysis.

Assumptions:

1) At high overpotentials the reverse reactions are negligible.
2) Eq. B-1 is in pseudo-equilibrium as Eq. B-2 is the rds.
3) Diffusion effects are negligible.
4) Hydrogen is adsorbed on active sites.
5) For the Langmuir isotherm, the reaction constants are independent of coverage (e.g. k=const.).
6) For the Frunkim-Temkin isotherm, the reaction constants are coverage dependent (e.g. k=f(θ)).

a) Langmuir analysis:

\[ i_1 = F\vec{k}_1(1 - \theta)e^{-\beta_1\nu f} - F\vec{k}_1\theta c_{OH}e^{(1-\beta_1)\nu f} \]  

\[ i_2 = F\vec{k}_2\theta^2 - F\vec{k}_2(1 - \theta)c_{H_2} \]

b) Frumkin-Temkin analysis:

\[ i_1 = F\vec{k}_1(1 - \theta)\theta^{1/2} - F\vec{k}_1\theta c_{OH}e^{-\beta_1\nu f} \]  

\[ i_2 = F\vec{k}_2\theta^2 - F\vec{k}_2(1 - \theta)c_{H_2} \]
Following the assumptions 1 and 2, $i_1=0$ and the reverse reaction in the Eq. B-4 is negligible. One has
\[ \frac{\theta}{1-\theta} = K_1 c_{OH} e^{-V_f} \] \hspace{1cm} (B-5)

And
\[ i_2 = F \tilde{k}_2 \theta^2 \] \hspace{1cm} (B-6)

where, $K_1 = \tilde{k}_1 / \tilde{k}_1$, $f = F/RT$ and $V = \eta + V_{\text{rev}}$.

For the special case where $\theta << 0.1$, then $\theta/(1-\theta)$ becomes $\theta$.

Introducing the Eq. B-5 in B-6 for $\theta << 0.1$

\[ i = F \tilde{k}_2 (K_1 c_{OH} e^{-V_f})^2 \] \hspace{1cm} (B-7)

One could rewrite this Eq. (B-7) as
\[ V = \frac{1}{2f} \left( \ln F \tilde{k}_2 K_1^2 c_{OH} - \ln i \right) \] \hspace{1cm} (B-8)

Partially deriving the Eq. B-8, the Tafel slope is obtained from the Langmuir approach as shown in the Eq. B-9
\[ \frac{\partial \eta}{\partial \ln i} = -\frac{RT}{2F} \] \hspace{1cm} (B-10)

b) Frunkim-Temkin analysis:

This analysis in similar to the Langmuir analysis, the only difference is that the dependence of the rate constants on the coverage factor is introduced as
\[ \tilde{k}_2 = k_{2,0} e^{2(1-\gamma)r\theta/RT} \] \hspace{1cm} (B-11)

And
\[ r\theta = \text{const} - VF \] \hspace{1cm} (B-12)

Considering $\gamma = 1/2$, and modifying $k_{2,0}$ such as it includes the $V_{\text{rev}}$ from $V$, then
\[ i = F k_{2, \theta=0} e^{-\eta F / RT} \]  

Deriving the Eq. B-13 partially, the Tafel slope is obtained as

\[ \frac{\partial \eta}{\partial \ln i} = -\frac{RT}{F} \]  

It can be seen that Eq. B-10 and B-14 are the solutions of two different approaches which model the same reaction mechanism.

4. Hydrogen evolution reaction (HER) analysis by electrochemical impedance spectroscopy (EIS).

We have included this explanation for EIS analysis of data form the HER on catalysts surfaces with simple chemical terms to aid the examiners to comprehend the discussions of the results that we have provided about electrochemical impedance for the HER.

Fig. B-1 shows the universally accepted HER mechanism for the HER, we have not included the Tafel step. The catalyst surface becomes negatively charge and attracts positively charged particles such as hydrogen ions (H\(^+\)), the positively partial charged end of the water molecules (a partial charge is created due to the asymmetric distribution of electrons in chemical bonds) and other inert positively charged particles that for the effects of our discussion are not of interest.
In the Volmer step, a water dipole is in contact with the surface, later the water molecule splits into an adsorbed hydrogen ion on the catalyst surface (i.e. M-H) with the release of one hydroxyol ion (\(\text{OH}^-\)). In the case of the Heyrovsky step, a M-H molecule reacts with water to produce one molecule of hydrogen, one \(\text{OH}^-\) ion and one free or empty active site of the catalyst (M). Every time that there is a charge transfer when an electron participates in the reaction, there is a consumption of energy which is represented as an electric resistance (e.g. charge transfer resistance \(R_{\text{ct}}\)).

In Fig. B-1, Volmer or Heyrovsky can be rate determining steps (rds) based on the properties of the catalyst, current density \((i)\), temperature of the reaction, etc. For example, if Volmer is rds then it would be a slower step than Heyrovsky and it should be expected that water would cover most of the catalyst surface, although some portion of adsorbed hydrogen can be present as well. This can be seen as a waiting queue, when boarding a plane at an airport, the slowest substation will have the longest queue, as for example, during checking in.
The accumulation of negative charges on the surface of the catalyst generates an electric field. Positively charged particles move toward the catalyst surface by the force applied to them ($\vec{F}$) with a magnitude described by Eq. B-15.

$$\vec{F} = q\vec{E}$$  \hspace{1cm} B-15

Where:

$\vec{F}$ : external force applied on a particle with electric charge (N).

$\vec{E}$ : electric field created on the surface of the catalyst (N/C).

$q$: electric charge of the particle (C).

The electric field generated on the surface of the catalyst can be considered as the electric field between two charged parallel plates. Eq. B-16 describes the magnitude of the electric field. Where; $\sigma$ is the charge density (i.e. quantity of electrons per unit of area) and $\varepsilon$ is the permittivity of the medium, which is water in our case.

$$E = \frac{\sigma}{\varepsilon}$$  \hspace{1cm} B-16

When an external force acts upon a particle, this will experience acceleration. The acceleration the particle experiences is described by Eq. B-17. Where, $m$ is the particle mass and $a$ is the acceleration. It can be seen from Eq. B-17 that heavier particles require more force to accelerate.

$$\vec{F} = m\vec{a}$$  \hspace{1cm} B-17

The acceleration a hydrogen particle experiences is described by combining Eqs. B-16 and B-17. The motion of a charged particle or the collective motion of charged
particles is detected as a signal by the EIS instrument. The motion of a charged particle generates a change in the magnetic and or electric field as shown in Fig. B-5.

Once the fundamentals have been explained, the next step is to understand the principle of operation of the EIS and combine this information with different scenarios found on the catalyst. Fig. B-2 shows the principle of operation of an EIS instrument. The HER is analysed at a constant working potential ($E_{WE}$) and wave amplitude ($V_a$) for a generic cycle $n$. A cycle is completed when the EIS instrument changes from low to high frequencies.

![EIS Principle of Operation for a Cycle $n$.](image)

Analysing data from different frequencies is key as distinctive interactions on the surface of the catalyst are detected at certain ranges of frequencies. Fig. B-3 shows three types of interactions which happen at different distinctive wave frequencies. In Fig. B-3 can be seen that a low frequencies, the mass transfer impedance manifests, at intermediate frequencies the charge transfer impedance appears and at high frequency the impedance from the oxide layer is observed. It should be noted that negative charges can accumulate in the interior of the catalyst only when the catalyst
is a semiconductor. Catalysts with low electric resistance such as electric conductors cannot accumulate charge in their interior, only on their surface.

![Diagram showing types of interactions found for the HER on the catalyst surface.](image)

Fig. B-3 Types of Interactions Found for the HER on the Catalyst Surface Sorted by Wave Frequency.

When the frequency of the wave is changed as illustrated in Fig. B-2, a change of the electric field is induced and can be seen as \( \frac{dE}{dt} \) (i.e. change of the electric field as a function of time). The electric field becomes proportional to the wave frequency. When the electric field changes, a particle or collection of similar particles will accelerate or change their location. In this respect, why different interactions are detected at different frequencies as shown in Fig. B-3?

Heavier particles require more impulse to experience a detectable translation or change of location. When a force is applied at a specific direction for longer times then heavier particles will experience motion. This concept is illustrated in Fig. B-4.
Considering the analysis of the EIS wave based on one unit of time, for low and high frequencies, it can be seen that the change of potential is above the $E_{we}$ line for the whole period of time only for the case at low frequency. Having the change of potential in the same direction for the entire period of time, will change the electric field in the same direction for a longer time and this will give more impulse to heavy particles. This is the reason why heavy particles, like ions are detected at low frequencies.

![Diagram of EIS Side of the Wave when it is Above $E_{we}$ for the Cycle $n$, at Low and High Frequencies for the Same Period of Time.](image)

Low mass particles like electrons, require substantially less impulse to experience motion, this is the reason why they are detected at high frequencies (cf. Fig. B-3). In the case of charge transfer, the hydrogen is constrained on the surface of the catalyst as it is adsorbed (cf. Fig. B-3). A different type of motion is seen for free hydrogen ions (determined at low frequencies) and adsorbed hydrogen ions (determined at intermediate frequencies). The following section gives further insight about capacitive and inductive behaviour found during the study of the HER by EIS.
4.1. Volmer and Heyrovsky competing for the rds

Fig. B-5 shows the origin of the capacitive and inductive behaviour found for the charge transfer impedance. As previously explained when Volmer is the rds, then a dominant ratio between the left and right side of the reaction expected (cf. Fig B-1). When Volmer is the rds, more water dipoles are expected to be on the catalyst surface than adsorbed hydrogen atoms. Fig. B-5 is a simplified illustration of the rds concept.

A Change in the electric field will change the amount of negative charges, this behaviour is capacitive in nature as for example capacitors with water as a dielectric.

Water dipole

A Change in the electric field will move the dipole $\delta^+,\delta^-$. Dipole motion is inductive in nature as for example moving magnets.

Fig. B-5 Capacitive and Inductive Behaviour of the HER as a Function of the rds
(Simplified Case).

A change in the electric field will change the quantity of electric charge and this is capacitive in nature. On the other side, motion of dipoles as for the case when Heyrovsky is the rds will generate a change in the magnetic field, which is inductive in nature. This is the reason that a low Tafel slopes (i.e. Heyrovsky as rds), inductive
behaviour can be seen as adsorbed hydrogen is in a higher concentration on the
catalyst surface than water dipoles.

References

2. Cogger, N. D.; Evans, N. J. An Introduction to Electrochemical
   Impedance Measurement; Solartron Analytical: 1999.
Appendix C

This appendix contains the covers of the published work from this research:


Hydrogen Generation

Dario Delgado, Glenn Hefter and Manickam Minakshi

Abstract The idea of an economy supported by hydrogen is still being considered by government bodies and major oil companies. The extensive use of hydrogen as a fuel has many applications in pollution-free technologies which could be of every-day use in society. Examples are in transportation and power generation; other uses include chemical technology, metallurgy, effluent processing and water production. For mass application the most appropriate process for hydrogen production is water electrolysis. To this end, a simplified description of the hydrogen and oxygen evolution mechanisms is presented. Understanding these mechanisms will provide a basis for making water electrolysis more efficient. For this reason special attention is given to the design of catalysts for water electrolysis.

1 Hydrogen Economy

The term ‘hydrogen economy’ was first coined by Bockris and Triner in 1970 [1], and it has been seen as a solution to the problems arising from the current unsustainable fossil fuel economy. Important contributions such as those by Meadows [2], Hubbert [3] and others [4], have supported the establishment of hydrogen as an alternative source of energy.

In recent years, the idea of the hydrogen economy becoming significant in the energy market has started to receive attention. The energy outlooks of the top oil

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Abstract  Undoubtedly, hydrogen will play an important role in the energy sector in the near future, in particular, as a fuel for transportation. However, electrolytic hydrogen generation is energy intensive and the means to save energy have been widely studied, as for example, the use of proton exchange membranes to minimize the voltage drop across the electrolyte. This research focuses in developing inexpensive alternative anode materials for oxygen generation in order to substitute expensive conventional anodes such as dimensionally stable anodes (DSA®). The geometric and electronic factors of the starting ‘electrolytic manganese dioxide (EMD) material’ are modified to enhance its electrochemical activity toward the oxygen evolution reaction. This has been achieved while using different dopants as additives during electrodeposition of MnO₂. The linear voltammetry and electrochemical impedance spectroscopy (EIS) analysis showed an increase in the surface area for the modified EMD (MEMD). X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) associated with elemental analysis (energy-dispersive X-ray spectroscopy (EDS)) illustrate a change in the oxygen composition and acidity which is correlated to the changes in electronic factor of the EMD. These results elucidate the improvement in overpotential observed for MEMDs when compared to that of DSA® at the current density of 100 mA cm⁻².

Keywords  EMD · Oxygen evolution · Electrochemistry · Hydrogen
Co/Mo bimetallic addition to electrolytic manganese dioxide for oxygen generation in acid medium

Dario Delgado¹, Manickam Minakshi¹, Justin McGinnity² & Dong-Jin Kim²

An efficient electrocatalyst comprising inexpensive and earth-abundant materials for the oxygen evolution reaction (OER) is crucial for the development of water electrolysis. In this work, in-situ addition of cobalt/molybdenum ions to the electrolytic manganese dioxide has been shown to be beneficial for the OER in acid solution as its overpotential performed better (305 mV) than that of the commercial DSA® (341 mV) at 100 mA cm⁻². The OER was investigated at ambient temperature in 2 M H₂SO₄ solution on the modified EMD (MnMoCoO) electrodes. The energy efficiency of the MnMoCoO electrodes improved significantly with the amount of Co in the plating solution. For the electrodeposited catalysts, physico-chemical and electrochemical measurements were conducted including static overpotentials. The better performance of the modified EMD was attributed to an improved charge transfer resistance (Rct; 0.290 Ω cm²), average roughness factor (rf; 429) and decrease in water content in the electrodeposited catalysts. The kinetic parameters obtained on MnMoCoO catalysts were compared and discussed according to the cobalt concentration.

Hydrogen is an abundant, renewable and clean energy source and has been considered as a solution to the problems arising from the current unsustainable fossil fuel economy. Recently, the hydrogen economy is gaining the attention of government bodies and major oil companies¹⁻⁸. Hydrogen can be generated through various methods including thermochemical, electrochemical and biochemical⁹. Of all these available methods, water electrolysis (via electrochemical) is suitable for large scale production of hydrogen. Electrolysis of water is a simple way to produce hydrogen with high purity at an economical price when a source of energy to drive the electrolysis is available such as solar or nuclear energy¹⁰.

The water electrolysis consists of two electrochemical reactions, termed as hydrogen and oxygen evolution reactions (HER and OER). The equilibrium potential of water electrolysis is 1.23 V at standard conditions but to drive the electrolysis at a practical rate requires higher potentials and this is conventionally measured as overpotential¹⁰. The difference between the equilibrium potential and the potential at practical current densities (e.g. 100 mA cm⁻²) is called polarization or overpotential (ψ). Metals such as Pt and Ru provide an excellent catalytic surface in lowering the overpotential (ψ) for the HER¹⁰. The most notable catalysts belong to the platinum group metals and are used for the HER, in addition, platinum group oxides¹¹⁻¹³ are used for the OER. However, platinum group metals are greatly limited by its scarcity and high cost. For instance, technologies such as fuel cells cannot be scaled up because they require expensive catalysts. The most efficient electrocatalyst for the OER are metal oxide electrodes¹²,¹³ (RuO₂ being the best¹³, IrO₂ also shows good overpotentials¹¹). Oxides present advantages over metal counterparts because they are more stable and cannot be further oxidized. Hence, the desire is to develop an inexpensive noble metal free OER catalyst.

With this as an objective, in our current paper, the use of electrolytic manganese dioxide (EMD, γ type MnO₂) with in-situ addition of cobalt/molybdenum ions during electrodeposition (termed modified...
The hydrogen economy has gained increasing attention from government bodies and major oil companies. There are proven examples of this technology being implemented in a society like Iceland, where electrolytic hydrogen generation powered by renewable energy has been developed to support the demand of the transportation sector. Hydrogen generation via electrolysis consists of the hydrogen and oxygen evolution reactions. Conventional electrode materials used for the electrolysis belong to the platinum group metals that are expensive. In this work, Raney cobalt as an alternative which is inexpensive, electrodeposited from a Watts bath is reported. In addition, modifying the Watts bath composition and combining two types of Raney have also been investigated and reported. We have identified overpotentials of -349 mV for the best Raney cobalt sample and -270 mV when Raney nickel is combined with Raney cobalt for hydrogen evolution in alkaline medium at 100 mA cm\(^{-2}\). Another objective of this work is resolving the difficulties found in interpreting the electrochemical impedance data for Raney type materials. The nickel binder competes with Raney cobalt during the reaction, these interactions exhibit different impedances. The electrodeposited electrodes have been tested for energy efficiency with overpotential curves and electrochemical impedance measurements. Additional tests including X-ray diffraction and field emission scanning electron microscopy equipped with energy dispersive analysis have also been undertaken that support the results of the catalyst surfaces under study.

**Keywords:** modified Watts Bath, Raney cobalt, hydrogen evolution.

1. **INTRODUCTION**

Recently, hydrogen has received increased attention from major oil companies like Exxon Mobil [1], Shell [2, 3] and BP [4]. Hydrogen is a source of energy to support society. These oil companies, in their energy outlook reports, point out a more diversified future for energy supply mix in