Lecture 4

Oxidative water splitting at metal oxide electrodes (SOWC’s)
The Hydrogen Economy: Hydrogen as an energy carrier.

Electrical power sources are connected to two electrodes which are placed in water:

- **Anode (oxidation OER):**
  \[ 2 \text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4 \text{H}^+(aq) + 4e^- \]

- **Cathode (reduction HER):**
  \[ 2 \text{H}^+(aq) + 2e^- \rightarrow \text{H}_2(g) \]

Usually ‘easy’

**OER**

Mostly difficult

**HER**
Cathodic Hydrogen Evolution Reaction (HER)

\[
\text{Acid: } 2H_3O^+ + 2e^- \rightarrow H_2(g) + 2 H_2O \\
\text{Base: } 2H_2O + 2e^- \rightarrow H_2(g) + 2 OH^-
\]

Simplest (therefore most studied) representative electro-catalytic reaction. Multistep process involving adsorbed intermediates.

**Volmer** (V): hydrogen adsorption or discharge step.
\[
H_3O^+ + M + e^- \rightarrow MH_{\text{ads}} + H_2O \\
H_2O + M + e^- \rightarrow MH_{\text{ads}} + OH^-
\]

**Heyrovsky** (H): Electrochemical Desorption step.
\[
MH_{\text{ads}} + H_3O^+ + e^- \rightarrow H_2(g) + M + H_2O \\
MH_{\text{ads}} + H_2O + e^- \rightarrow H_2(g) + M + OH^-
\]

**Tafel** (T): Chemical Desorption step.
\[
MH_{\text{ads}} + MH_{\text{ads}} \rightarrow H_2(g) + 2M
\]

2 main mechanisms:
- **Volmer–Heyrovsky** (VH)
- **Volmer–Tafel** (VT).

Classical analysis assumes HER occurs on oxide free metal surface. However some metal oxide films are Stable under active HER conditions.
Anodic Oxygen Evolution Reaction (OER)

- Kinetically limiting step in water electrolysis cells and PEM fuel cell.
- Multistep multi-electron transfer reaction involving adsorbed intermediates.
- Overall reaction (alkaline medium)
  \[ O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^- \]
  \[ E^0 = 0.303 \text{ V (vs. Hg/HgO)} \]

- Krasil'shchikov (1963)
  \[ S + OH^- \rightleftharpoons SOH_{ad} + e^- \]
  \[ SOH_{ad} + OH^- \rightleftharpoons SO_{ad}^- + H_2O \]
  \[ SO_{ad}^- \rightleftharpoons SO_{ad} + e^- \]
  \[ 2SO_{ad} \rightarrow 2S + O_2 \]

- Bockris Electrochemical Oxide (1956)
  \[ S + OH^- \rightleftharpoons SOH_{ad} + e^- \]
  \[ SOH_{ad} + OH^- \rightleftharpoons SO + H_2O + e^- \]
  \[ SO + SO \rightleftharpoons 2S + O_2 \]

- Depending on RDS can explain a variety of Tafel slopes.
- Modification permits concept of formation/decomposition of higher oxide - e.g. for Ni
  \[ O\text{H}^- \rightleftharpoons O\text{H}_{ad} + e^- \]
  \[ O\text{H}_{ad} + OH^- \rightleftharpoons O_{ad}^- + H_2O \]
  \[ 2 \beta\text{-NiOOH} + O_{ad}^- \rightleftharpoons 2\text{NiO}_2 + H_2O + e^- \]
  \[ 2\text{NiO}_2 + H_2O \rightleftharpoons 2 \beta\text{-NiOOH} + O_{ad} \]
  \[ O_{ad} + O_{ad} \rightarrow O_2 \]

- OER at oxidized metal and metal oxide electrodes involves active participation of oxide.
- Acid/base behaviour of oxide important.
- Concept of active surface or surface groups important.

Anodic OER process is much more complex and kinetically challenging than cathodic HER. We focus attention on OER process at oxidized metal and metal electrodes.
Electrolytic generation of molecular di-oxygen

- Kinetically limiting step in water electrolysis cells and Electrowinning cell.
- Multistep multi-electron transfer reaction involving adsorbed intermediates.
- Need to understand details of Oxygen Evolution Reaction (OER) in order to optimize process at electrode surface.
- Depending on RDS can explain a variety of Tafel slopes.
- Key mechanistic parameters are: Tafel Slope and reaction order wrt proton/hydroxide ion activity.
- OER at oxidized metal and metal oxide electrodes involves active participation of oxide.
- Acid/base behaviour of oxide important consideration.
- Concept of active surface or surface groups important.
### Anodic Oxygen Evolution Reaction (OER)

**Table 2.** Kinetic parameters derived for 5 most common OER mechanisms [169].

<table>
<thead>
<tr>
<th>Rate-determining step</th>
<th>Langmuir</th>
<th>Temkin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma$</td>
<td>$\theta \rightarrow 0$</td>
</tr>
<tr>
<td>(I) Bockris's Oxide Path</td>
<td>4</td>
<td>2RT/F</td>
</tr>
<tr>
<td>1. $M + OH^- \rightarrow MOH + e^-$</td>
<td>2</td>
<td>RT/2F</td>
</tr>
<tr>
<td>2. $2MOH \rightarrow MO + M + H_2O$</td>
<td>2</td>
<td>RT/3F</td>
</tr>
<tr>
<td>(II) Bockris's Electrochemical Path</td>
<td>2</td>
<td>2RT/F</td>
</tr>
<tr>
<td>1. $M + OH^- \rightarrow MOH + e^-$</td>
<td>2</td>
<td>RT/3F</td>
</tr>
<tr>
<td>2. $2MO \rightarrow 2M + O_2$</td>
<td>1</td>
<td>RT/4F</td>
</tr>
<tr>
<td>(III) Krasil' shchikov's Path</td>
<td>2</td>
<td>RT/3F</td>
</tr>
<tr>
<td>1. $M + OH^- \rightarrow MOH + e^-$</td>
<td>2</td>
<td>RT/4F</td>
</tr>
<tr>
<td>2. $2MOH \rightarrow MO + H_2O + e^-$</td>
<td>1</td>
<td>RT/4F</td>
</tr>
<tr>
<td>(IV) O'Grady's Path</td>
<td>2</td>
<td>2RT/F</td>
</tr>
<tr>
<td>1. $M^2+ + OH^- \rightarrow M^2OH + e^-$</td>
<td>2</td>
<td>RT/3F</td>
</tr>
<tr>
<td>2. $2M^2OH \rightarrow M^2OH + e^-$</td>
<td>1</td>
<td>RT/4F</td>
</tr>
<tr>
<td>(V) Kobussen's Path</td>
<td>2</td>
<td>RT/3F</td>
</tr>
<tr>
<td>1. $M + OH^- \rightarrow MOH + e^-$</td>
<td>1</td>
<td>RT/2F</td>
</tr>
<tr>
<td>2. $2MOH \rightarrow MO + M + H_2O + e^-$</td>
<td>1</td>
<td>RT/3F</td>
</tr>
<tr>
<td>(VI) Krasil'shchikov's Path</td>
<td>2</td>
<td>RT/3F</td>
</tr>
<tr>
<td>1. $M + OH^- \rightarrow MOH + e^-$</td>
<td>2</td>
<td>RT/4F</td>
</tr>
<tr>
<td>2. $2MOH \rightarrow MO + H_2O + e^-$</td>
<td>1</td>
<td>RT/3F</td>
</tr>
<tr>
<td>(VII) Krasil'shchikov's Path</td>
<td>2</td>
<td>RT/3F</td>
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<tr>
<td>1. $M + OH^- \rightarrow MOH + e^-$</td>
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<td>(IX) Krasil'shchikov's Path</td>
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<td>1</td>
<td>RT/3F</td>
</tr>
</tbody>
</table>

* Symmetry factors, i.e. $B$, $y$, and $z$, in all steps, were taken as $1/6$. * Stoichiometric number. * $\theta$ is the potential difference between the outer Helmholtz plane and the bulk of the solution. * Nonactivated desorption of O$_2$. * Activated desorption of O$_2$. * $r$ is a coefficient determining the variation of heat of adsorption of a particular species with coverage. Unless stated, $r$ values for each species were taken as equal. $K_i$ is the equilibrium constant of the $i$th step. * $r_i$ and $r_2$ refer to $r$ for $M^2OH$ and $r$ for $M^3OH$, respectively.

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Rhodium redox chemistry: alkaline solution

Microdispersed hydrous oxide formed via potential cycling technique (similar to poly(aniline) deposition to form PME).


Duplex layer model: oxide/solution interface.
OER at multicycled hydrous rhodium oxide modified electrodes.

Fig. 1. Cyclic voltammograms (0.05 V s⁻¹ sweep rate) for a rhodium electrode in 1.0 mol dm⁻³ NaOH after being subjected to various numbers of potential sweeps (0-1.55 V, 0.15 V s⁻¹). Numbers refer to potential sweeps.

Fig. 2. Effect of thick oxide growth on the iR plots for oxygen evolution at 88 in 1.0 mol dm⁻³ NaOH at 25°C. Number of oxide growth cycles (0-1.55 V, 3.0 V s⁻¹): (○) 0, (△) 20, (□) 120, (●) 600, (◇) 2100; (◇) 4500.

OER activity & mechanism (shift in OER potential and decrease in Tafel slope) depends on charge capacity (thickness) of hydrous oxide layer.

Anodic OER TEECE Group Activity

- Focus to date on kinetic and mechanistic studies on anodic OER for alkaline water electrolysis.

- Attention on oxidized transition metals, transition metal oxide coated electrodes (hydrous, electro-precipitated and thermally prepared).

- To date materials focus has been directed towards following systems:
  - Electrochemically prepared passive and hydrous Iron, Nickel, Cobalt oxy-hydroxide films.
  - Electrodeposited Ni(OH)\textsubscript{2} films on Au, GC and Pt support surfaces.
  - Thermally prepared single component oxides: NiO, RuO\textsubscript{2}, IrO\textsubscript{2}, Co\textsubscript{3}O\textsubscript{4}, MnO\textsubscript{2}, on Ti and Ni support electrodes
  - Thermally prepared (from inorganic precursor salts annealed in air) mixed oxides: Ru\textsubscript{x}Sn\textsubscript{1-x}O\textsubscript{2}, Ru\textsubscript{x}Ir\textsubscript{1-x}O\textsubscript{2}, RuO\textsubscript{2}/Co\textsubscript{3}O\textsubscript{4}, Ru\textsubscript{x}Ti\textsubscript{1-x}O\textsubscript{2}, Ir\textsubscript{x}Sn\textsubscript{1-x}O\textsubscript{2}.

- Future attention on range of binary/ternary mixed DSA and nanostructured type metal oxides based on RuO\textsubscript{2} and IrO\textsubscript{2} incorporating cheap inactive metal oxides

  - Electro-catalytic kinetics and mechanism with respect to anodic OER at Ni and Fe electrodes in aqueous base evaluated and quantified.

  - Novel anodic water splitting OER mechanism proposed involving surf-aquo groups in hydrous oxide layer. OER onset potential depends on acid/base properties of hydrous oxide layer.

  - Currently developing molecular scale model for detailed OER pathway in terms of interlinked surf-aquo group model.

  - Fe and Ni oxide materials are cheap and effective electrode materials for anodic water splitting.

  - Next stage is to examine application of these oxide materials to Cathodic Oxygen Reduction Reaction (ORR) and hydrogen evolution reaction (HER). The latter topics are currently unexplored at hydrous oxide materials.

  - Extending analysis to metal oxide films prepared via thermal decomposition of precursor & via sol/gel routes.
Pre-reduction at $E = -1.30\text{V}$ for $t = 15\text{ min}$, followed by 1 cycle between $-1.175$ and $0.625\text{ V}$ in $1.0\text{ M NaOH}$ at $40\text{ mV/s}$.

**Fig. 12** Typical voltammetric profile for an aged iron electrode (see text for more details) recorded in $1.0\text{ M NaOH}$ at $40\text{ mV/s}$.

**Fig. 14** Reaction order plots based upon the polarisation curves of Fig. 13, at the indicated potentials.

**Fig. 13** iR-corrected steady state polarisation curves recorded in the direction of increasing potential for an aged iron electrode (as characterised voltammetrically in Fig. 12) in NaOH solutions of various concentration.

Oxidized metal electrode (not multicycled)

**Lyons & Brandon 2009**

Aged electrode, severe cathodic pre-treatment: OER Kinetic parameters

**Low overpotentials**

$b = 60\text{ mV dec}^{-1} = 2.303(\text{RT/F})$

$m_{\text{OH}^-} = 3/2$

**High overpotentials**

$b = 120\text{ mV dec}^{-1} = 2.303(2\text{RT/F})$

$m_{\text{OH}^-} = 1.0$
**OER Kinetic Analysis: Model A**
Lyons 1984

\[ S + OH^- \rightarrow SOH + e^- \]  
(AI)

\[ SOH + OH^- \rightarrow SO^- + H_2O \]  
(AII)

\[ SO^- + OH^- \rightarrow SO_2H^+ + e^- \]  
(AIII)

\[ SO_2H^+ + OH^- \rightarrow S + H_2O + O_2 + 2e^- \]  
(AIV)

\[ S = \text{electrocatalytically active iron surface group = stabilized Fe(VI) moiety} \]

**QSSA, Langmuir Adsorption conditions:**

\[
i = \frac{4Fk_1^0k_2a_Sa_{OH}^2 \exp[\beta F \eta/RT]}{k_1^0 \exp[-(1-\beta)F \eta/RT] + k_2a_{OH}}
\]

\[
i \approx 4Fk_1^0a_Sa_{OH} \exp[\beta F \eta/RT]
\]

\[
i \approx 4Fk_2a_Sa_{OH}^2 \left\{\frac{k_1^0}{k_{-1}}\right\} \exp[F \eta/RT]
\]

Simple Kinetic analysis (Lyons 1984) predicts Correct Tafel slopes over entire \( \eta \) range, but predicts a reaction order \( m_{OH} \) of 2 at low \( \eta \) (instead of 3/2) and 1 at high \( \eta \).

Dual Tafel Slope behaviour attributed to change in RDS as potential increases.
\[ S + OH^- \rightarrow S-OH + e^- \]  
(BI)

\[ S-OH + OH^- \rightarrow S-H_2O_2 + e^- \]  
(BII)

\[ S-H_2O_2 + OH^- \rightarrow S-OH^- + H_2O \]  
(BIII)

\[ S-H_2O_2 + S-HO_2^- \rightarrow O_2 + H_2O + OH^- \]  
(BIV)

\[ S-H_2O_2 = \text{physisorbed hydrogen peroxide} \]

Assume intermediate surface coverage of S-OH species. Pseudo-equilibrium condition & Temkin adsorption isotherm (interaction parameter \( g_{ij} \)) assumed.

Assume at low \( \eta \) step (BII) is rate limiting.

\[ f_\Sigma \equiv k_2^0a_{OH}\theta_{SOH} \exp \left[ \left(1-\gamma \right)\frac{g_{SOH}\theta_{\Sigma} - \gamma g_{SH2O2}\theta_{\Sigma}}{RT} \right] \exp \left[ \frac{\beta F\eta}{RT} \right] \]

\[ f_\Sigma \equiv k_2^0a_{OH}\theta_{SOH} \exp \left[ \left(1-\gamma \right)\frac{g_{SOH}\theta_{\Sigma}}{RT} \right] \exp \left[ \frac{\beta F\eta}{RT} \right] \]

Assume step (BI) is in pseudo-equilibrium.

\[ f_i = f_{-1} \]

\[ f_i = k_i^0a_{OH} \left(1 - \theta_{SOH}\right) \exp \left[ - \frac{g_{SOH}\theta_{\Sigma}}{RT} \right] \exp \left[ \frac{\beta F\eta}{RT} \right] \]

\[ f_{-1} = k_{-1}^0\theta_{SOH} \exp \left[ \left(1-\gamma \right)\frac{g_{SOH}\theta_{\Sigma}}{RT} \right] \exp \left[ - \left(1-\beta \right)F\eta \right] \]

\[ \left\{ \begin{array}{l} \theta_{SOH} \\ 1-\theta_{SOH} \end{array} \right\} \exp \left[ \frac{g_{SOH}\theta_{\Sigma}}{RT} \right] \equiv \exp \left[ \frac{g_{SOH}\theta_{\Sigma}}{RT} \right] = k_i^0k_{-1}a_{OH} \exp \left[ \frac{F\eta}{RT} \right] = K_{a_{OH}} \exp \left[ \frac{F\eta}{RT} \right] \]

\[ g_{SOH}\theta_{\Sigma} \equiv RT \ln \left( K_{a_{OH}} \right) + F\eta \]

\[ S-H_2O_2 = \text{physisorbed hydrogen peroxide} \]

\[ \sum \frac{\partial \eta}{\partial \log f_\Sigma} = 2.303 \frac{RT}{\left(1-\gamma + \beta \right)F} \]

\[ \eta \rightarrow \frac{2.303RT}{F} \]

\[ m_{OH} = \left( \frac{\partial \ln f_\Sigma}{\partial \ln a_{OH}} \right)_\eta = 2 - \gamma \frac{2}{3/2} \]

At high \( \eta \) surface coverage conditions change to where \( \theta_{SOH} = \theta_{\Sigma} \rightarrow 1 \). Step (BII) still rate determining. Langmuir adsorption pertains. Also \( g_{SOH} \rightarrow 0 \).
OER Kinetics: Aged (EC polarization measurements) pre-reduced Fe electrodes (not multicycled).

Peak A₄ becomes more enhanced on aging. Compact anhydrous oxide chemistry dominates interfacial EC behaviour. Is associated with increase in low overpotential Tafel slope from ca. 40 mV to ca. 45-47 mV.

Pre-treatment: cathodic polarization at E = -1.10V in 1.0 M NaOH, t = 5 min, followed by single cycle at 40 mV/s between limits -1.175 to 0.625 V.
OER Kinetics: Aged pre-reduced Fe electrodes (not multicycled).

Cyclic voltammograms (1.0 M NaOH, scan rate = 40 mV s\(^{-1}\)) characterising an Fe electrode prior to its 1\(^{st}\), 5\(^{th}\) and 16\(^{th}\) utilisation in OER polarisation experiments.

Effect of oxide on OER Kinetics at oxidized aged Fe explained in terms of Conway-Meyer dual barrier model.

\[
\begin{align*}
[\text{Fe(VI)}O_{m}(OH)_{n}]^{p-} + OH^- & \rightarrow [\text{Fe(VI)}O_{m+1}(OH)_{n-1}]^{p-} + H_2O + e^- \\
[\text{Fe(VI)}O_{m+1}(OH)_{n-1}]^{p-} + OH^- & \rightarrow [\text{Fe(VI)}O_{m}OOH(OH)_{n-1}]^{p-} + e^- \quad \text{RDS}
\end{align*}
\]

\[
\begin{align*}
[\text{Fe(VI)}O_{m}OOH(OH)_{n-1}]^{p-} + OH^- & \rightarrow [\text{Fe(VI)}O_{m}OO(OH)_{n-1}]^{p-} + H_2O + e^- \\
[\text{Fe(VI)}O_{m}OO(OH)_{n-1}]^{p-}+ OH^- & \rightarrow [\text{Fe(VI)}O_{m}(OH)_{n}]^{p-} + O_2 + e^- \\
p = 2m+n-6 & \quad b \approx 2.303 \times 4RT/5F \quad m_{OH} \approx 1
\end{align*}
\]

Physisorbed peroxide intermediate model assumed.

OER steady state polarisation curves for a pre-reduced Fe electrode in various NaOH solutions. The trace denoted as “fresher 1.0 M” was recorded for the same electrode in an earlier experiment, before satisfactory reproducibility with respect to Tafel slope had become established.

Inset - Reaction order plots constructed from the reproducible polarisation data at a potential of \(E = 0.7\) V.

Low overpotential
Conway-Meyer Dual Barrier Model

Potential dependent field assisted charge transfer across a barrier oxide film (process F) in series with interfacial charge transfer reaction (process S). Effective Symmetry factor (and hence Tafel slope) and reaction order is some fraction $F(\beta) = \beta_F/(\beta_F + \beta_S)$ of the true values.

$\beta_\Sigma \equiv F(\beta)\beta_S = \left(\frac{\beta_F}{\beta_F + \beta_S}\right)\beta_S$

$b_{\text{eff}} \equiv F(\beta)^{-1}b_S$

$m_{t,\text{eff}} \equiv F(\beta)m_{t,s} = \left(\frac{\beta_F}{\beta_F + \beta_S}\right)m_{t,s}$

Effective reaction order

Reaction order in absence of barrier

**Aged pre-reduced Fe electrodes**

**OER Kinetic analysis**

**Incorporating DBM.**

\[ S + OH^- \rightarrow S-OH + e^- \]  
\[ S-OH + OH^- \rightarrow S-H_2O_2 + e^- \]  
\[ S-H_2O_2 + OH^- \rightarrow S-OH_2^- + H_2O \]  
\[ S-H_2O_2 + S-HO_2^- \rightarrow O_2 + H_2O + OH^- \]  

Assume step (BII) is rate determining (low \( \eta \) values), and that dual barrier model pertains. Analysis of barrier free situation suggests that \( b_S = 40 \text{ mV/dec} \) and \( m_{OH} = 2. \)

\[
\begin{align*}
\beta_f & = 2.303 \frac{RT}{F(1 + \beta_F \beta_S)} \\
\beta_s & = 2.303 \frac{4RT}{5F} = 0.047 \text{ V/dec} \\
m_{OH,eff} & = \frac{2\beta_F}{\beta_F + \beta_S} m_{OH} = \frac{2\beta_F}{\beta_F + \beta_S} \beta_F = \beta_S = 1/2 \\
& \rightarrow 1
\end{align*}
\]

Low overpotentials

Assume step (BI) is rate determining (high \( \eta \) values), and that dual barrier model pertains. Analysis of barrier free situation suggests \( b_S = 0.120 \text{ V/dec} \) and \( m_{OH} = 1.0. \)

\[
\begin{align*}
\beta_f & = 2.303 \frac{RT}{\beta_S F} \\
\beta_s & = 2.303 \frac{4RT}{F} = 0.235 \text{ V/dec} \\
m_{OH,eff} & = \frac{\beta_F}{\beta_F + \beta_S} m_{OH} = \frac{\beta_F}{\beta_F + \beta_S} m_{OH} = \beta_F = \beta_S = 1/2 \\
& \rightarrow 1/2
\end{align*}
\]

High overpotentials

Not easy to check this prediction at high \( \eta. \)
# Electrode Experiment, $b, m_{OH}^-$

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Dual barrier</th>
<th>b, $m_{OH}^-$ for analysis</th>
<th>Isotherm L or T</th>
<th>Pathway</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni no-pre-treat</td>
<td>No</td>
<td>As listed left</td>
<td>L, $\theta \rightarrow 0$</td>
<td>C</td>
</tr>
<tr>
<td>Ni pre-reduced</td>
<td>No</td>
<td>As listed left</td>
<td>L, $\theta \rightarrow 0$</td>
<td>C</td>
</tr>
<tr>
<td>Ni pre-oxidised</td>
<td>No</td>
<td>As listed left</td>
<td>L, $\theta \rightarrow 0$</td>
<td>C</td>
</tr>
<tr>
<td>Co no-pre-treat</td>
<td>Low $[OH^-]$</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Co pre-reduced</td>
<td>Yes</td>
<td>2RT/3F, 2</td>
<td>L, $\theta \rightarrow 0$</td>
<td>E</td>
</tr>
<tr>
<td>Co aged low $\eta$</td>
<td>No</td>
<td>As listed left</td>
<td>T, $r_I \gg r_{II}$</td>
<td>E</td>
</tr>
<tr>
<td>Co aged high $\eta$</td>
<td>No</td>
<td>As listed left</td>
<td>L, $\theta \rightarrow 1$</td>
<td>E</td>
</tr>
<tr>
<td>Fe no-pre-treat</td>
<td>No</td>
<td>As listed left</td>
<td>L, $\theta \rightarrow 1$</td>
<td>-----</td>
</tr>
<tr>
<td>Fe pre-reduced (fresh)</td>
<td>No</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Fe pre-reduced (aged)</td>
<td>Yes</td>
<td>2RT/3F, 2</td>
<td>L, $\theta \rightarrow 0$</td>
<td>E</td>
</tr>
<tr>
<td>Fe aged low $\eta$</td>
<td>No</td>
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<td>T, $r_I \gg r_{II}$</td>
<td>E</td>
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<td>Fe aged high $\eta$</td>
<td>No</td>
<td>As listed left</td>
<td>L, $\theta \rightarrow 1$</td>
<td>E</td>
</tr>
</tbody>
</table>
Electrochemical Impedance Spectroscopy: Oxidized metal films anodic OER

![Image of EIS experiment](image)

Fig. 17 Equivalent circuits used in the CNLS fitting of the impedance data of Fig. 15 and 16. Circuit A reduces to Circuit B at higher overpotentials and the latter is used for modelling the data recorded at 0.76 and 0.8 V. The meaning of $R_{\text{ct}}$ is discussed below (see eqn (9)).

Pseudo Tafel Plot from EIS Experiments

![Image of Pseudo Tafel Plot](image)

Fig. 18 Log $(R_{\text{ct}})^{-1}$ vs. $\eta$ plots constructed from the impedance data of Fig. 15.
Lyons Brandon
Physisorbed peroxide
OER model incorporating Dual Barrier concept.

Interlinked surface groups

Hydrous Oxide Layer

Compact Oxide Layer

It is well established that thermally prepared RuO$_2$ films exhibit three distinct redox processes involving Ru$^{IV/IV}$, Ru$^{IV/VI}$ and Ru$^{VI/VII}$ surface redox transitions. The latter transformation which occurs at elevated anodic potentials prior to the onset of active oxygen gas evolution is most marked in base.

We would therefore expect that the surface redox chemistry of a mixed oxide such as Ir$_x$Ru$_{1-x}$O$_2$ in which both components are electroactive, would exhibit rather complex voltammetric behaviour.

The chemistry of anhydrous iridium oxide involves a major charge storage Ir$^{III/IV}$ transition and an Ir$^{IV/VI}$ transition prior to the onset of active oxygen evolution.
Catalytic DSA MUDCRACK Morphology.

Fig. 2. (a) AFM micrographs of RuO$_2$ electrodes prepared from RuO$_2$ by thermal decomposition at 325°C and 450°C. Scale width: 20 µm. (b) Width-height line/scatter at the 325°C RuO$_2$ electrode. Scale width: 100 µm x 200 µm. Average line thickness: 5.05 µm.

Fig. 5 SEM micrographs of an RuO$_2$-TiO$_2$ coated Ti electrode. (a) ×200, (b) ×600. The characteristic 'cracked' morphology is evident.
Surfaquo group concept

- Metal oxide surfaces in contact with aqueous solutions have a significant hydrophilic character. As an oxide interacts with water solvent molecules become bonded to the metal cations which exhibit Lewis acidity resulting in the transfer of a proton to a neighbouring oxygen site.
- Un-dissociated water molecules may also be present. Hence the oxide surface is extensively hydroxylated. It has been determined that only oxycations at certain sites (presumably sites of low coordination such as kink or ledge sites) are capable of participating in the redox reactions giving rise to the peaks observed in the recorded voltammetric response.
- The important factor seems to be the ability of the latter type of cations to extensively coordinate water molecules. Inactive ruthenium or iridium species would exhibit a higher degree of oxygen bridging type coordination and would presumably exist along terrace sites.

- These ideas emphasizing the important role of hydration in determining the difference between active and inactive surface bonded groups led to the designation of the former as surfaquo groups.
- Although the structure of such active surfaquo groups is unknown it is very likely that the linkage to the surface involves one or more oxygen bridges to generate the following type of hydrous species (the bridging oxygen species being represented here by \(-O-\)):

\[
\begin{align*}
(-O-)_{2}RuO_2(OH)_2 & \leftrightarrow (-O-)_{2}RuO(OH)(OH) \leftrightarrow (-O-)_{2}Ru(OH)_4
\end{align*}
\]

Ru(VI) surfaquo groups

Fig. 9. Sketch of an oxide/aqueous solution interface.
Surfaquo group redox Chemistry: RuO$_2$ surface.

\[ (-O-)_{2}RuO_{2}(OH_{2})_{2} \leftrightarrow (-O-)_{2}RuO(OH)(OH_{2}) \]
\[ \leftrightarrow (-O-)_{2}Ru(OH)_{4} \]

OER Mechanism acid medium 1 M H$_2$SO$_4$

\[ (-O-)_{2}Ru(OH)(OH_{2})_{3} \rightarrow (-O-)_{2}Ru(OH)_{2}(OH_{2})_{2} + H^+ + e^- \]
\[ Ru^{III/IV}: (-O-)_{2}Ru(OH)(OH_{2})_{2} \rightarrow (-O-)_{2}Ru(OH)_{4} + 2H^+ + 2e^- \]
\[ Ru^{IV/VII}: (-O-)_{2}Ru(OH)_{4} \rightarrow (-O-)_{2}RuO(OH)_{3} + H^+ + e^- \]

OER Mechanism basic medium 1M NaOH

\[ (-O-)_{2}RuO(OH)(OH_{2})_{3} \leftrightarrow (-O-)_{2}RuO(OH)_{3} + H^+ + e^- \text{ fast} \]
\[ (-O-)_{2}RuO(OH)_{3} \rightarrow (-O-)_{2}RuO^{2+}O(OH_{2})_{3} + e^- \text{ slow rds} \]
\[ (-O-)_{2}Ru^{II+}O(OH)_{3} \leftrightarrow (-O-)_{2}RuO(OH)_{2} + O_2 + 2H^+ + 2e^- \text{ fast} \]
\[ (-O-)_{2}RuO(OH)_{2} + H_2O \leftrightarrow (-O-)_{2}Ru(OH)_{4} \text{ fast} \]

The chemistry of the OER is the chemistry of the surfaquo group.
Anodic OER, Multicycled Fe aqueous alkaline solution.

60 mV dec⁻¹ / 40 mV dec⁻¹ Tafel slope depends on base concentration/potential limits at which oxide layer is formed via RPM.

Linear Plot: \( \Delta E / \Delta i \) vs \( 1/i \)

\[
E = a + b \log i \\
\frac{dE}{di} = b \cdot \frac{1}{2.303i} + R_\text{i}A
\]

\( b = \text{Tafel Slope} \)
\( i = \text{current density} \)

Potential / V vs. Hg/HgO

Log (Current / A)

Charge Q / C cm⁻²

Current Density / A cm⁻²

Potential / V vs. Hg/HgO

Charge Q / C cm⁻²
Hydrous Iron Oxide Electrodes. OER Reaction Order Studies

N = 120 cycles
Reaction order wrt OH⁻ activity ca. 0.9 (low TS region) and ca. 0.8 (high TS region).

Measure OER current density at fixed overpotential from analysis of Tafel Plots as function of OH⁻ ion activity.
Ni in aqueous base: redox activity and OER behaviour.

Voltammetric response of hydrous Ni oxide film as function of base concentration.

E/V

Ni oxide layer grown in 1.0 M NaOH. N = 120 cycles.
Reaction order plot, low Tafel Slope Region.
$m_{\text{OH}^-} = 0.85$.

Low potential: TS = 60 mV/dec.
High potential: TS = 120 mV/dec

N = 120 cycles

Tafel Plots for OER at Ni oxide layers grown via potential cycling (N = 120 cycles) in 1.0 M NaOH recorded as function of base concentration.

Ni oxide layer grown in 1.0 M NaOH. N = 120 cycles.
Reaction order plot, high Tafel Slope Region.
$m_{\text{OH}^-} = 0.82$. 
Effect of oxide charge capacity Q on OER catalytic efficiency: Ni in aqueous base.

Tafel Plot OER as function of hydrous layer thickness (# cycles).

Variation of low overpotential Tafel Slope for OER at multicycled Ni oxide Electrode in 1.0 M NaOH as a function of oxide charge capacity Q (thickness).

Oxygen evolution rate at fixed potential at oxide coated Ni in 1.0 M NaOH as function of redox charge storage capacity of hydrous layer.

EIS Measurements: Hydrous iron oxide film

EIS data

Metal oxide film becomes more conducting with increasing potential.
• At OER overpotentials where simple Tafel behaviour prevails:

\[ i = i_0 \exp \left( \frac{2.303 \eta}{b} \right) \]

Differentiating gives:

\[ \frac{dI}{d\eta} = \frac{2.303 i_0 b}{I_0} \exp \left( \frac{2.303 \eta}{b} \right) \]

Noting that \( dI/d\eta = dI/dE = 1/R_{\text{far}} \):

\[ \log \left( \frac{1}{R_{\text{far}}} \right) = \frac{E}{b} - \log \left( \frac{2.303 i_0}{b} \right) \]

• EIS Tafel slope 66 mV dec\(^{-1}\)

• Good agreement with steady-state polarisation Tafel slope of 60 mV dec\(^{-1}\).
Tafel Plots OER, alkaline solutions. Electro-precipitated Nickel oxy-hydroxide thin films deposited via CPM on Au supports.

OER onset overpotential decreases with increasing base concentration.
Low potential Tafel slope for OER at electro-precipitated nickel oxyhydroxide film grown on Au support via CPM, as function of $\text{OH}^-$ concentration.

Limiting low potential $\text{TS} = 47 \text{ mV/ dec}$

$N = 30 \text{ cycles } SR = 50 \text{ mV s}^{-1}$ Plating medium: 0.1 M NiSO$_4$, 0.1 M NaAc.3H$_2$O, 0.001 M KOH CPM : - 900, + 1200 mV (vs SCE), 50 mVs$^{-1}$. 
High potential Tafel slope for OER at electro-precipitated nickel oxyhydroxide film grown on Au support via CPM, as function of OH$^-$ concentration.
Reaction order plot. Electroprecipitated Nickel oxy-hydroxide thin films.

$m_{OH^-} = 1.12$
OER Mechanism at Fe & Ni oxyhydroxide modified electrodes

\[ \text{SOH}_2 + \text{OH}^- \rightleftharpoons \text{SOH}^- + \text{H}_2\text{O} \]
\[ \text{SOH}^- \rightarrow \text{SOH} + e^- \]
\[ \text{SOH} + \text{OH}^- \rightarrow \text{SO}^- + \text{H}_2\text{O} \]
\[ \text{SO}^- \rightarrow \text{SO} + e^- \]
\[ \text{SO} + \text{OH}^- \rightarrow \text{SOOH} + e^- \]
\[ \text{SOOH} + \text{OH}^- \rightarrow \text{SO}_2 + \text{H}_2\text{O} + e^- \]
\[ \text{SO}_2 + \text{OH}^- \rightarrow \text{O}_2 + \text{SOH}^- \]

DFT calculations being initiated to generate quantitative Energy Landscape for OER Mechanism.

Mechanism valid for multicycled & electroprecipitated M = Fe & Ni. Explains Tafel Slope & reaction order data.

Similar mechanism applicable for DSA films

OER mechanism involving surfaquo groups in the hydrous oxy-metal hydroxide layer.
An atlas of electrochemical reactivity for anodic OER

Electro-precipitated $\beta$-Ni(OH)$_2$ : The 'right' type of oxide for OER

We have succeeded in preparing very effective catalytic electrodes for anodic OER using very cheap Materials (nickel oxide).

All currents (OER rate) scaled to voltammetric charge which is proportional to real surface area.
An atlas of electrochemical reactivity for anodic OER

Tafel Plots IR corrected and normalised wrt real surface area S measured via electrochemical capacitance measurement.

Electro-precipitated $\beta$-Ni(OH)$_2$ : The 'right' type of oxide for OER

Current DSA state of art
Concluding Comments

• Reproducible and scalable methodology developed for generation of hydrated Fe & Ni metal oxide thin films and electroprecipitated nickel oxyhydroxide films on Au, GC and Pt supports in aqueous base.

• Duplex layer model proposed for structure of oxide/solution interface region.

• Hydrous oxide thin films exhibit super-Nernstian shifts in redox potential with respect to changes in solution pH value. Implying commercial spinoff potential for new generation metal wire pH sensors for use in biomedical applications.

• Dynamics of redox switching in hydrous oxide layer quantified via Aoki Model.

• Electro-catalytic kinetics and mechanism with respect to anodic OER at Ni and Fe electrodes in aqueous base evaluated and quantified.

• Novel anodic water splitting OER mechanism proposed involving surfaquo groups in hydrous oxide layer. OER onset potential depends on acid/base properties of hydrous oxide layer.

• Currently developing molecular scale model for detailed OER pathway in terms of interlinked surfaquo group model.

• Fe and Ni oxide materials are cheap and effective electrode materials for anodic water splitting.

• Next stage is to examine application of these oxide materials to Cathodic Oxygen Reduction Reaction (ORR) and hydrogen evolution reaction (HER). The latter topics are currently unexplored at hydrous oxide materials.

• Extending analysis to metal oxide films prepared via thermal decomposition of precursor & via sol/gel routes.