Development of new catalysts for water electrolysis

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Development of new catalysts for water electrolysis

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Symposium
Water electrolysis and hydrogen as part of the future Renewable Energy System
Outline

✓ Motivation
✓ Theoretical trends in oxygen evolution activity
✓ Corrosion protection mechanism
✓ Films preparation- Sputter deposition
✓ Nanoparticles- Cluster source
✓ Summary
Motivation

Renewable sources → Electrical energy → Fuel Cells/Electrolysers → Chemical energy $\text{H}_2$ → PEM

$\text{H}_2\text{O} \leftrightarrow \frac{1}{2} \text{O}_2 + \text{H}_2$
Motivation

Limitations of the efficiency of a PEM electrolyser

\[ E_{\text{cell}} = E_0 + \eta_{\text{anode}} + \eta_{\text{cathode}} + \text{IR} \]

Theoretical trends in oxygen evolution activity

Ideal catalyst

\[ \Delta G [\text{eV}] \]

- \(2\text{H}_2\text{O}(l)\)
- \(\text{HO}^* + \text{H}_2\text{O}(l)\)
- \(\text{O}^* + \text{H}_2\text{O}(l)\)
- \(\text{HOO}^* + 3(\text{e}^- + \text{H}^+)\)
- \(\text{O}_2(g) + 4(\text{e}^- + \text{H}^+)\)

\(\Delta G = 1.23 \text{ eV}\)
Theoretical trends in oxygen evolution activity

RuO$_2$ (110)
Theoretical trends in oxygen evolution activity

Composition of the earth crust

O, Si, Al, Fe, Ca, Na, Mg, K, Ti → 98.8%

Ru → 1E-7 %
Ir → 3E-8 %
Mn → 0.095%
Theoretical trends in oxygen evolution activity

\[ \text{H}_2\text{O} + * \rightarrow \text{HO}^* + \text{H}^+ + \text{e}^- \quad \Delta G_1 \]

\[ \text{HO}^* \rightarrow \text{O}^* + \text{H}^+ + \text{e}^- \quad \Delta G_2 \]

\[ \text{O}^* + \text{H}_2\text{O} \rightarrow \text{HOO}^* + \text{H}^+ + \text{e}^- \quad \Delta G_3 \]

\[ \text{HOO}^* \rightarrow \text{O}_2 + \text{H}^+ + \text{e}^- \quad \Delta G_4 \]

Scaling relations:

\[ \Delta E_{\text{HOO}} = \Delta E_{\text{HO}} + 3.2 \text{ eV} \]

Descriptor of the oxygen evolving activity: \( \Delta G_{\text{O}^*} - \Delta G_{\text{HO}^*} \)

Volcano plots

Perovskites, rutiles, anatase, \( \text{Mn}_x\text{O}_y \), \( \text{Co}_3\text{O}_4 \), \( \text{NiO} \)
Theoretical trends in oxygen evolution activity

Volcano plots for oxides

Garcia-Mota and col, Chem Cat Chem 3 (2011) 1159
Theoretical trends in oxygen evolution activity

MnO\(_2\) → Stable from 1.1 to 1.7V at pH1

η\(_{\text{MnO}_2}\) → 0.61 V

η\(_{\text{RuO}_2}\) → 0.37 V

η\(_{\text{IrO}_2}\) → 0.57 V

How to protect MnOx from corrosion

Mann I., Thesis, 2010, DTU Physics
Protection from corrosion

↑ activity (η = 0.42V @10mA/cm²)

↓ corrosion resistance (1.4 V at pH1)

↓ activity (η = 0.58V @10mA/cm²)

↑ corrosion resistance (2.1 V at pH1)

RuO₂, IrO₂

Mann I., Thesis, 2010, DTU Physics
Protection from corrosion

IrO$_2$ + 2H$_2$O $\leftrightarrow$ IrO$_4^{2-}$ + 4H$^+$ + 4e$^-$ $U_0$ = 2.057 V
RuO$_2$ + 3H$_2$O $\leftrightarrow$ H$_2$RuO$_4$ + 4H$^+$ + 4e$^-$ $U_0$ = 1.4 V

Ir segregates to the kink sites

Ir should be placed on the kink sites to protect Ru from corrosion

Mann, I. Thesis, 2011, DTU Physics
Film preparation - Sputter deposition

- **MnO\textsubscript{x}-1**
  - 90 nm Mn at 5 mTorr Ar and 480°C
  - 100 W
  - Annealed in air at 480°C (Furnace)

- **MnO\textsubscript{x}-2**
  - 1.5 nm Ti
  - 90 nm MnO\textsubscript{x} at 3 mTorr Ar/O\textsubscript{2} (10sccm) and 150°C
  - 100 W
  - Annealed in air at 480°C (Furnace)
Film preparation- Sputter deposition

OER activity in N₂ sat. 0.1M KOH
1600 rpm  5mV/s

Table 1. Oxygen Electrode Activities

<table>
<thead>
<tr>
<th>Catalyst Material</th>
<th>ORR: E(V) at ( l = -3 \text{ mA} \cdot \text{cm}^{-2} )</th>
<th>OER: E(V) at ( l = 10 \text{ mA} \cdot \text{cm}^{-2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 wt % Ir/C</td>
<td>0.69</td>
<td>1.61</td>
</tr>
<tr>
<td>20 wt % Ru/C</td>
<td>0.61</td>
<td>1.62</td>
</tr>
<tr>
<td>20 wt % Pt/C</td>
<td>0.86</td>
<td>2.02 (1.88)</td>
</tr>
<tr>
<td>Mn oxide</td>
<td>0.73</td>
<td>1.77 (1.88)</td>
</tr>
</tbody>
</table>

1.8V \text{RHE} @ 10 mA/cm²
1.73 V \text{RHE} @ 5 mA/cm²
MnOx-1

1.66 V \text{RHE} @ 5 mA/cm²

Jaramillo et al., JACS 132 (2010) 13612
Film preparation - Sputter deposition

MnOx-1 SEM MnOx electrodeposited

Corrosion protection → Acidic media

Jaramillo et al, JACS 132 (2010) 13612
Nanoparticles- Cluster source

- Size varies from 1 atom to 10 nm.
- Size is a function of the power and gas flow.
- STM
- TPD
- ATM
- SEM
- LEED
- ISS
- TEM
Nanoparticles- Cluster source

OER activity in N$_2$ sat. 0.1M HClO$_4$
1600 rpm  20mV/s

Ru NP 4nm

0.07 $\mu$g$_{Ru}$
Nanoparticles - Cluster source

Strasser et al., Electrochim Solid St Lett 13 (2010) B36

Ru NP 4nm → 1344 mA/mg_{Ru} @1.48V
Ru NP 4nm → 1344 A/g_{Ru} @1.48V

Corrosion protection
**Summary**

- RuO$_2$ is the most active catalysts for OER, but we need to protect it from corrosion → Ir on the kink sites

- MnO$_2$ is a good candidate to replace RuO$_2$ because is active and abundant

- The catalytic activity of the MnO$_2$ films prepared by sputter deposition are comparable with the state of the art (alkaline)

- The mass activity of the Ru NP prepared in the cluster source is one order of magnitude higher than the state of the art
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Patricia Hernández-Fernández¹, Elisa A. Paoli¹, Rasmus Frydendal¹, Ifan E.L. Stephens¹, Jan Rossmeisl², Ib Chorkendorff¹

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Theoretical trends in oxygen evolution activity

RuO$_2$ vs ideal catalyst
Theoretical trends in oxygen evolution activity

Ideal catalyst

\[
\begin{align*}
\Delta G [\text{eV}] & \\
-1 & \quad 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \\
2\text{H}_2\text{O}(l) & \\
\text{HO}^*+\text{H}_2\text{O}(l) & +e^-+\text{H}^+ \\
\text{O}^*+\text{H}_2\text{O}(l) & +2(e^-+\text{H}^+) \\
\text{HOO}^* & +3(e^-+\text{H}^+) \\
\text{O}_2(g) & +4(e^-+\text{H}^+) \\
U=0 \text{ V} & 
\end{align*}
\]
Theoretical trends in oxygen evolution activity

\[ \text{RuO}_2 \ (110) \]
Theoretical trends in oxygen evolution activity

Free energy diagram:

\[ \Delta G_3 - \Delta G_2 \sim 3 \text{ eV} \rightarrow O^* \text{ position} \]

- \[ \text{HO}^* \rightarrow O^* + H^+ + e^- \quad \Delta G_2 \]
- \[ O^* + H_2O \rightarrow \text{HOO}^* + H^+ + e^- \quad \Delta G_3 \]

\[ \eta_{\text{RuO}_2} \rightarrow 0.37 \text{ V} \]
\[ \eta_{\text{IrO}_2} \rightarrow 0.57 \text{ V} \]
\[ \eta = 0.61 \text{ V} \]

Rossmeisl and col, Chem Cat Chem 3 (2011) 1159