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

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

Renewable sources → Electrical energy

Fuel Cells ↔ Electrolysers

Chemical energy $\text{H}_2$ ↔ $\frac{1}{2} \text{O}_2 + \text{H}_2$

PEM
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

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

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

\[ \text{U}=0 \text{ V} \]

1.23 eV
Theoretical trends in oxygen evolution activity

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

Composition of the earth crust

O, Si, Al, Fe, Ca, Na, Mg, K, Ti $\rightarrow$ 98.8%

- Ru $\rightarrow$ 1E-7 %
- Ir $\rightarrow$ 3E-8 %
- Mn $\rightarrow$ 0.095%
**Theoretical trends in oxygen evolution activity**

\[
\begin{align*}
H_2O + * & \rightarrow HO^* + H^+ + e^- \quad \Delta G_1 \\
HO^* & \rightarrow O^* + H^+ + e^- \quad \Delta G_2 \\
O^* + H_2O & \rightarrow HOO^* + H^+ + e^- \quad \Delta G_3 \\
HOO^* & \rightarrow O_2 + H^+ + e^- \quad \Delta G_4
\end{align*}
\]

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

**Scaling relations:**

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

**Volcano plots**

- Perovskites, rutiles, anatase, Mn\(_x\)O\(_y\), Co\(_3\)O\(_4\), NiO
- Too strong
- Too weak

\[
\Delta G_{O^*} - \Delta G_{HO^*}
\]
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

Manganese

MnO₂ → Stable from 1.1 to 1.7V at pH1

η₉ = 0.61 V
η_{RuO₂} → 0.37 V
η_{IrO₂} → 0.57 V

How to protect MnOx from corrosion

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

↑ activity ($\eta = 0.42\text{V @10mA/cm}^2$)

↓ corrosion resistance (1.4 V at pH1)

RuO$_2$ + IrO$_2$

↓ activity ($\eta = 0.58\text{V @10mA/cm}^2$)

↑ corrosion resistance (2.1 V at pH1)

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

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

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 480C
  - 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 150C
  - 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

1.8V_{RHE} @ 10 mA/cm²
1.73 V_{RHE} @ 5 mA/cm²

MnOx-1

1.66 V_{RHE} @ 5 mA/cm²

Table 1. Oxygen Electrode Activities

<table>
<thead>
<tr>
<th>Catalyst Material</th>
<th>ORR: E(V) at ( l = -3 ) mA·cm⁻²</th>
<th>OER: E(V) at ( l = 10 ) mA·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)²</td>
</tr>
<tr>
<td>Mn oxide</td>
<td>0.73</td>
<td>1.77</td>
</tr>
</tbody>
</table>

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 10nm
- Size is function on 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

\[ j \text{ (mA/cm}^2\text{)} \]
\[ U(V) \text{ vs RHE} \]

Ru NP 4nm

0.07 \( \mu g_{\text{Ru}} \)
Nanoparticles- Cluster source


Ru NP 4nm $\rightarrow$ 1344 mA/mg$_{Ru}$ @1.48V  
Ru NP 4nm $\rightarrow$ 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 $\rightarrow$ 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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Theoretical trends in oxygen evolution activity

RuO$_2$ vs ideal catalyst

\[ \Delta G [eV] \]

- Optimal
- RuO$_2$

\[ \begin{align*}
S_0 + 2H_2O(l) &\quad \rightarrow \quad S_1 \\
S_1 &\quad \rightarrow \quad S_2 \\
S_2 &\quad \rightarrow \quad S_3 \\
S_3 &\quad \rightarrow \quad S_0 + O_2(g)
\end{align*} \]

\[ + e^- + H^+ \]

\[ +2(e^- + H^+) \]

\[ +3(e^- + H^+) \]

\[ +4(e^- + H^+) \]

U = 0 V
Theoretical trends in oxygen evolution activity

Ideal catalyst

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

- \( 2H_2O(l) \)
- \( HO^*+H_2O(l) + e^-+H^+ \)
- \( O^*+H_2O(l) + 2(e^-+H^+) \)
- \( HOO^*+3(e^-+H^+) \)
- \( O_2(g) + 4(e^-+H^+) \)

\( U=0 \text{ V} \)
Theoretical trends in oxygen evolution activity

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

Free energy diagram:

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

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

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

\[ \eta_{\text{RuO}_2} \rightarrow 0.37 \text{ V} \]

\[ \eta_{\text{IrO}_2} \rightarrow 0.57 \text{ V} \]

\[ \eta = 0.61 \text{ V} \]

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