Development of new catalysts for water electrolysis

Hernandez-Fernandez, Patricia; Paoli, Elisa Antares; Frydendal, Rasmus; Stephens, Ifan; Rossmeisl, Jan; Chorkendorff, Ib

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Development of new catalysts for water electrolysis

Patricia Hernández-Fernández¹, Elisa A. Paoli¹, Rasmus Frydendal¹, Ifan E.L. Stephens¹, Jan Rossmeisl², Ib Chorkendorff¹

¹Center for Individual Nanoparticle Functionality,
²Center for Atomic-scale Materials Design Technical University of Denmark

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 $H_2$

$H_2O \leftrightarrow \frac{1}{2}O_2 + H_2$

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

\[ \Delta G [eV] \]

\[ \begin{align*}
2H_2O(l) & \rightarrow 2H^+ + 2e^- + H_2O(l) \\
HO^* + H_2O(l) & \rightarrow O^* + H_2O(l) + e^- + H^+ \\
HOO^* + 3(e^- + H^+) & \rightarrow O_2(g) + 4(e^- + H^+) \\
\end{align*} \]

1.23 eV

U = 0 V
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

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

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

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

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

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

Scaling relations:

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

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

**Manganese**

\[ \text{MnO}_2 \rightarrow \text{Stable from 1.1 to 1.7V at pH1} \]

\[ \eta_\text{MnO}_2 \rightarrow 0.61 \text{ V} \]

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

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

How to protect MnOx from corrosion

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

↑ activity ($\eta = 0.42\text{V} @ 10\text{mA/cm}^2$)
↓ corrosion resistance (1.4 V at pH1)

RuO$_2$ - IrO$_2$

↓ activity ($\eta = 0.58\text{V} @ 10\text{mA/cm}^2$)
↑ corrosion resistance (2.1 V at pH1)

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

\[ \text{IrO}_2 + 2\text{H}_2\text{O} \leftrightarrow \text{IrO}_4^{2-} + 4\text{H}^+ + 4\text{e}^- \quad U_0 = 2.057\text{V} \]

\[ \text{RuO}_2 + 3\text{H}_2\text{O} \leftrightarrow \text{H}_2\text{RuO}_4 + 4\text{H}^+ + 4\text{e}^- \quad U_0 = 1.4\text{V} \]

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 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 N$_2$ sat. 0.1M KOH
1600 rpm  5mV/s

- $1.8V_{\text{RHE}}$ @ 10 mA/cm$^2$
- $1.73V_{\text{RHE}}$ @ 5 mA/cm$^2$

MnOx-1

Jaramillo et al., JACS 132 (2010) 13612

<table>
<thead>
<tr>
<th>Catalyst Material</th>
<th>ORR: $E(V)$ at $I = -3$ mA·cm$^{-2}$</th>
<th>OER: $E(V)$ at $I = 10$ 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)$^a$</td>
</tr>
<tr>
<td>Mn oxide</td>
<td>0.73</td>
<td>1.77</td>
</tr>
</tbody>
</table>

$1.66V_{\text{RHE}}$ @ 5 mA/cm$^2$
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 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

$\mu$g$_{\text{Ru}}$ 0.07

Ru NP 4nm
Nanoparticles - Cluster source


Ru NP 4nm → 1344 mA/mg$_{\text{Ru}}$ @1.48V

Ru NP 4nm → 1344 A/g$_{\text{Ru}}$ @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

Theoretical trends in oxygen evolution activity

Ideal catalyst

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

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

U = 0 V
Theoretical trends in oxygen evolution activity

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

Free energy diagram:

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

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

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

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

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

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