Development of new catalysts for water electrolysis

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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

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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 $\text{H}_2$

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

PEM

CAMd
Center for Atomic-scale Materials Design
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]

$2H_2O(l)$

$\text{HO}^* + H_2O(l) + e^- + H^+$

$\text{O}^* + H_2O(l) + 2(e^- + H^+)$

$\text{HOO}^* + 3(e^- + H^+)$

$O_2(g) + 4(e^- + H^+)$

1.23 eV

U=0 V

0
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

H₂O + * → HO* + H⁺ + e⁻  ΔG₁

HO* → O* + H⁺ + e⁻  ΔG₂

O* + H₂O → HOO* + H⁺ + e⁻  ΔG₃

HOO* → O₂ + H⁺ + e⁻  ΔG₄

Descriptor of the oxygen evolving activity: ΔG_{O*}-ΔG_{HO*}

Scaling relations:

ΔE_{HOO} = ΔE_{HO} + 3.2 eV

Volcano plots

Perovskites, rutiles, anatase, MnₓOᵧ, Co₃O₄, NiO

3.2 eV
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

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

$\eta_{\text{RuO}_2} \rightarrow 0.37 \text{ V}$

$\eta_{\text{IrO}_2} \rightarrow 0.57 \text{ V}$

How to protect MnOx from corrosion

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

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

RuO$_2$\(\rightarrow\)IrO$_2$

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

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

IrO₂ + 2H₂O ⇌ IrO₄²⁻ + 4H⁺ + 4e⁻  \( U_0 = 2.057 \text{V} \)
RuO₂ + 3H₂O ⇌ H₂RuO₄ + 4H⁺ + 4e⁻  \( U_0 = 1.4 \text{V} \)

Ir segregates to the kink sites

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

\( U = U_0 - 0.1 \text{V} \)

\( U = U_0 + 0.6 \text{V} \)

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

- **MnO$_x$-1**
  - 90 nm Mn at 5 mTorr Ar and 480°C
  - 100 W
  - Annealed in air at 480°C (Furnace)

- **MnO$_x$-2**
  - 1.5 nm Ti
  - 90 nm MnO$_x$ at 3 mTorr Ar/O$_2$ (10 sccm) and 150°C
  - 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

1.8$V_{\text{RHE}}$ @ 10 mA/cm$^2$
1.73 $V_{\text{RHE}}$ @ 5 mA/cm$^2$
1.66 $V_{\text{RHE}}$ @ 5 mA/cm$^2$

MnOx-1

**Table 1. Oxygen Electrode Activities**

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<th>Catalyst Material</th>
<th>ORR: E(V) at I = −3 mA·cm$^{-2}$</th>
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<td>0.69</td>
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<td>20 wt % Pt/C</td>
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Jaramillo et al., JACS 132 (2010) 13612

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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, TEM, ISS, LEED, SEM, TPD.

**Magnetron sputter source**

Support (GC)
Nanoparticles - Cluster source

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

Ru NP 4nm
Nanoparticles - Cluster source

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

Ru NP 4nm $\to$ 1344 mA/mg$_{\text{Ru}}$ @1.48V
Ru NP 4nm $\to$ 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 → 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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RuO$_2$ vs ideal catalyst

![Diagram showing the theoretical trends in oxygen evolution activity with RuO$_2$ vs ideal catalyst.](image_url)
Theoretical trends in oxygen evolution activity

Ideal catalyst

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

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

U=0 V

1.23 V
Theoretical trends in oxygen evolution activity

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

Free energy diagram:

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

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

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

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

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

\[ 3.11 \text{ (eV)} \]

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