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

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

ΔG [eV]

2H_2O(l) → O^* + H_2O(l) + e^- + H^+

HO^* + H_2O(l) → O^* + H_2O(l) + e^- + H^+

O^* + H_2O(l) → HO^* + H_2O(l) + e^- + H^+

HOO^* + 3(e^- + H^+) → 1.23 eV

O_2(g) + 4(e^- + H^+) → 1.23 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

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: ΔGₐ-O* - ΔGₐ-HO*

Scaling relations:

ΔE_{HOO} = ΔE_{HO} + 3.2 eV

Volcano plots

Perovskites, rutiles, anatase, MnₓOᵧ, Co₃O₄, 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

MnO$_2$ → $\eta$ = 0.61 V

$\eta_{\text{RuO}_2}$ → 0.37 V

$\eta_{\text{IrO}_2}$ → 0.57 V

How to protect MnOx from corrosion
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

IrO₂ + 2H₂O ⇌ IrO₄²⁻ + 4H⁺ + 4e⁻ \hspace{1cm} U₀ = 2.057V
RuO₂ + 3H₂O ⇌ H₂RuO₄ + 4H⁺ + 4e⁻ \hspace{1cm} U₀ = 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$_x$-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$^2$

MnOx-1

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

Jaramillo et al., JACS 132 (2010) 13612

Table 1. Oxygen Electrode Activities

<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>
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

Ru NP 4nm

$0.07 \mu g_{Ru}$
Nanoparticles - Cluster source


Ru NP 4nm → 1344 mA/mg\textsubscript{Ru} @1.48V

Ru NP 4nm → 1344 A/g\textsubscript{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

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

- \( 2H_2O(l) \)
- \( HO^* + H_2O(l) \)
- \( O^* + H_2O(l) \)
- \( HOO^* \)
- \( O_2(g) \)

\[ +3(e^- + H^+) \]
\[ +4(e^- + H^+) \]

U = 0 V
Theoretical trends in oxygen evolution activity

RuO₂ (110)
Theoretical trends in oxygen evolution activity

Free energy diagram:

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

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

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

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

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

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