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 $\text{H}_2$

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

**Electrolysers**

**Fuel Cells**

**Chemical energy $\text{H}_2$**

**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

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

\[2\text{H}_2\text{O(l)} \rightarrow \text{HO}^* + \text{H}_2\text{O(l)} + e^- + \text{H}^+ \] \hspace{1cm} 1.23 \text{ eV}

\[\text{HO}^* + \text{H}_2\text{O(l)} + 2(e^- + \text{H}^+) \rightarrow \text{O}^* + \text{H}_2\text{O(l)} \] \hspace{1cm} 1.23 \text{ eV}

\[\text{O}^* + \text{H}_2\text{O(l)} + 3(e^- + \text{H}^+) \rightarrow \text{HOO}^* + 4(e^- + \text{H}^+) \] \hspace{1cm} 1.23 \text{ eV}

\[\text{HOO}^* + 4(e^- + \text{H}^+) \rightarrow \text{O}_2(g) + 4(e^- + \text{H}^+) \] \hspace{1cm} 1.23 \text{ eV}

\[\text{O}_2(g) + 4(e^- + \text{H}^+) \rightarrow U = 0 \text{ V} \]
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

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

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

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

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

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, Mn\textsubscript{x}O\textsubscript{y}, Co\textsubscript{3}O\textsubscript{4}, 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$_2$ $\rightarrow$ Stable from 1.1 to 1.7V at pH1

$\eta$ $\approx$ 0.61 V

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

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

How to protect MnO$_x$ from corrosion
Protection from corrosion

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

RuO$_2$ $\cap$ 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

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<sub>x</sub>-1**
  - 90 nm Mn at 5 mTorr Ar and 480°C
  - 100 W
  - Annealed in air at 480°C (Furnace)

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

OER activity in N\textsubscript{2} sat. 0.1M KOH
1600 rpm 5mV/s

1.8\(V_{\text{RHE}}\) @ 10 mA/cm\textsuperscript{2}

1.73 \(V_{\text{RHE}}\) @ 5 mA/cm\textsuperscript{2}

MnOx-1

\[ j (\text{mA/cm}^2) \]

\[ U(V) \text{ vs RHE} \]

1.66 \(V_{\text{RHE}}\) @ 5 mA/cm\textsuperscript{2}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
\textbf{Catalyst} & \textbf{ORR: E(V) at} & \textbf{OER: E(V) at} \\
& \(l = -3 \text{ mA}\cdot\text{cm}^{-2}\) & \(l = 10 \text{ mA}\cdot\text{cm}^{-2}\) \\
\hline
20 wt \% Ir/C & 0.69 & 1.61 \\
20 wt \% Ru/C & 0.61 & 1.62 \\
20 wt \% Pt/C & 0.86 & 2.02 (1.88)\textsuperscript{a} \\
Mn oxide & 0.73 & 1.77 \\
\hline
\end{tabular}
\end{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 of the power and gas flow

- STM
- TPD
- ATM
- SEM
- LEED
- ISS
- TEM
Nanoparticles - Cluster source

OER activity in N\textsubscript{2} sat. 0.1M HClO\textsubscript{4} 
1600 rpm  20mV/s

Ru NP 4nm

0.07 \mu g_{Ru}
Nanoparticles- Cluster source


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

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

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

\[ \begin{align*}
2\text{H}_2\text{O}(l) & \rightarrow \text{HO}^*+\text{H}_2\text{O}(l) \\
\text{O}^*+\text{H}_2\text{O}(l) & \rightarrow \text{HOO}^* \\
\text{O}_2(g) & \rightarrow +4(e^-+H^+) \\
\end{align*} \]

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

\[ \begin{align*}
S_0+2\text{H}_2\text{O}(l) & \rightarrow +e^-+H^+ \\
S_1 & \rightarrow +2(e^-+H^+) \\
S_2 & \rightarrow +3(e^-+H^+) \\
S_3 & \rightarrow +4(e^-+H^+) \\
S_0+\text{O}_2(g) & \rightarrow U=0 \text{ V} \\
\end{align*} \]
Theoretical trends in oxygen evolution activity

Ideal catalyst

\[
\Delta G \ [eV]
\]

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

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

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

Free energy diagram:

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

Ideal catalyst:
- \( \eta_{\text{RuO}_2} \rightarrow 0.37 \text{ V} \)
- \( \eta_{\text{IrO}_2} \rightarrow 0.57 \text{ V} \)
- \( \eta = 0.61 \text{ V} \)

Equations:
- \( \text{HO}^* \rightarrow O^* + H^+ + e^- \quad \Delta G_2 \)
- \( O^* + H_2O \rightarrow \text{HOO}^* + H^+ + e^- \quad \Delta G_3 \)

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