Comparison of IrOx and IrRuOx oxides as anodic electrocatalysts for solid polymer electrolyte water electrolysis

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ElectroHypem Project

Enhanced performance and cost-effective materials for long-term operation of PEM water electrolysers coupled to renewable power sources - ELECTROHYPEM

(Contract number 300081)

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Oxide Electro catalysts under investigation

- $\text{Ir-oxide}$
- $\text{IrRu-oxide}$

- Synthesis by using Adams Fusion preparation routes
- Chemical, structural, surface and morphology properties
- Electrochemical testing
Ir$_{0.7}$Ru$_{0.3}$Ox Anode Electro-Catalyst

Adams Synthesis

(IrCl$_4$·H$_2$O + RuCl$_3$·H$_2$O + isopropanol) Solution – NaNO$_3$ mixture

Dry at 70°C

Calcination at 500°C/10 min

The fused salt – oxide mixture was washed and filtered three times with distilled water to remove the remaining salts

Dry in air at 90 °C/overnight

pre-leaching procedure (in HClO$_4$ 0.1 M, 80 °C, 15 min)

To completely remove the sodium impurities
**IrOx - Ir$_{0.7}$Ru$_{0.3}$Ox Anode Electro-Catalysts**

**Characterization**

A lattice contraction suggestive of the formation of a solid solution.
**IrOx - Ir$_{0.7}$Ru$_{0.3}$O$_x$ Anode Electro-Catalysts**

**Morphology**

**SEM**

SEM-EDX: IrO$_x$
(no impurities)

SEM-EDX: Ir$_{0.7}$Ru$_{0.3}$O$_x$ (70:30 at.%) 
(no impurities)
IrOx - Ir\textsubscript{0.7}Ru\textsubscript{0.3}O\textsubscript{x} Anode Electro-Catalysts

EDX analysis for elemental bulk composition

\begin{center}
\begin{tabular}{|c|c|c|}
\hline
 & Ir & Ru \\
\hline
IrOx & 100 & 0 \\
IrRuOx & 70 & 30 \\
\hline
\end{tabular}
\end{center}

Ir:Ru=70:30 in agreement with the nominal one.
Several particles show a rectangular shape and a significant fraction of these particles are faceted than round (spherical).

*The inset shows the crystalline lattice of the primary particles*

*The lattice lines was used to determine the size of the crystalline domains that was about 5.4 nm and 5.2 nm for the IrOx and IrRuOx, respectively*
No impurities are present on the surface.
The surface atomic composition was Ir:Ru=75:25 for the IrRuOx catalyst indicating a slight segregation of Ir on the surface. Whereas after sputtering with Ar\(^+\) ions the atomic composition of the mixed oxide catalyst was Ir:Ru=70:30 in good agreement with the nominal one.

The surface enrichment in Iridium versus bulk composition has been probably promoted by pre-leaching treatment in perchloric acid.
Electrochemical Characterization

Electrolysis Cell (5 cm²)

**Cathode:** 30%Pt/C (E-TEK) → loading ~ 0.5 mg/cm²
Deposition: *doctor blade*
30%Pt/C + Nafion 33%
carbon cloth backing (HT ELAT)

**Membrane:** Nafion 115

**Anode:** IrO₂ → loading ~ 1.5 mg/cm²
Deposition: *spray at 80°C*
IrO₂ + Nafion 20% on membrane
Ti grid was used as backing layer
IrO$_x$ – Nafion 115

80 °C: 0.7 A·cm$^{-2}$ @ 1.6 V
2 A·cm$^{-2}$ @ 1.8 V

80 °C: Rs 116 mΩ·cm$^2$
Rct 127 mΩ·cm$^2$
Ir$_{0.7}$Ru$_{0.3}$Ox – Nafion 115

**80 °C:**
- $1 \text{ A} \cdot \text{cm}^{-2}$ @ $1.6 \text{ V}$
- $2.4 \text{ A} \cdot \text{cm}^{-2}$ @ $1.8 \text{ V}$

**80 °C:**
- $R_s$ 110 mΩ · cm$^2$
- $R_{ct}$ 72 mΩ · cm$^2$
**IrO\textsubscript{x} - Ir\textsubscript{0.7}Ru\textsubscript{0.3}O\textsubscript{x} – Nafion 115 Comparison**

**30°C**

<table>
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<th>Catalysts</th>
<th>Potential / V</th>
<th>Current density / A cm\textsuperscript{-2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>IrO\textsubscript{2}</td>
<td>1.6</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>1.8</td>
<td>0.9</td>
</tr>
<tr>
<td>IrRuO\textsubscript{x}</td>
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<td>0.31</td>
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<td>1.8</td>
<td>1.1</td>
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</table>

**90°C**

<table>
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<th>Catalysts</th>
<th>Potential / V</th>
<th>Current density / A cm\textsuperscript{-2}</th>
</tr>
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<td></td>
<td>1.8</td>
<td>2</td>
</tr>
<tr>
<td>IrRuO\textsubscript{x}</td>
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<tr>
<td></td>
<td>1.8</td>
<td>2.8</td>
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</table>
This confirms that the presence of ruthenium in the catalyst improves the charge transfer for oxygen evolution in the electrolysis cell.
Similar slopes for both catalysts in the range of 60 - 80 mV/dec

The same Tafel slope would indicate a similar reaction mechanism; thus, being both particle size and morphology similar, the observed changes reflect a different intrinsic catalytic activity (larger electrochemical rate constant) as consequence of the different chemistry.

It should be considered that this Tafel slope also includes a small contribution of the hydrogen evolution electrode.
Activation energy for the electrochemical process is about 20% lower in the case of the mixed Ir-Ru oxide (39.5 kJ/mol) compared to IrOx (48.1 kJ/mol)
Conclusions

The present study demonstrates that Ir0.7Ru0.3Ox-based electrocatalyst is an excellent catalyst for the oxygen evolution in PEM-based water electrolysis provided that structure, morphology and surface characteristics are properly modulated.

ACKNOWLEDGEMENT

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