Cost Effective and Highly Active Catalysts for Anodes of Proton Exchange Membrane Electrolysis

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Contents

• Hydrogen as energy vector

• Cost and availability of iridium catalyst

• DLR activities in PEM Electrolysis

• Synthesis of $\text{IrO}_x$-Ir, Ir/SnO$_2$:Sb-aerogel, Ir$_{0.7}$Ru$_{0.3}$O$_2$ catalysts

• OER activity and stability

• Summary
Hydrogen as energy vector

• High percentage of renewable energy in energy supply chain need long-term storage facilities

• Intermittent oversupply of RE will increase significantly (in 2050 ~25 TWh will be available for hydrogen production in Germany)

1. Intermittent oversupply of RE from wind and sun
2. Feeding in electrical grid
3. Hydrogen production via electrolysis (3000-4000 hours per year)
4. Hydrogen can be distributed via the natural gas grid
5. Hydrogen can be used in industry and for heat production
6. Mobility for fuel cell-driven vehicles
PEM electrolysis: Working principle and cost breakdown

- Bipolar plates are the most expensive component (51%) of the stack
- Currently the cost of the PMG catalyst (Ir and Pt) comprise only 8%
- The real obstacle for industrial PEM electrolyzers are the lack of business cases and unsuitable H₂ regulations


\[ E_{\text{cell}} = 2 \text{ V}, \text{pH} = 0, 80 \degree \text{C} \]
Cost and availability of PEM electrolyzer catalysts

- Global iridium production of less than 9 t yr\(^{-1}\). 90% comes from South Africa.

- Current MEA specifications:
  - Anode: 2-3 mg\(_{\text{iridium}}\) cm\(^{-2}\)
  - Cathode: < 1 mg\(_{\text{platinum}}\) cm\(^{-2}\)

- 7530 tons of Ir are required for PEM electrolyzers operating at \(E_{\text{cell}} = 1.65\) V. It is equivalent to 836 times the annual production.

- Chemical, metal and refinery industries require hundreds of TW of H\(_2\).

PEM electrolysis technology is not scalable to the TW level!

DLR activities in PEM Electrolysis: from Fundamentals to Megawatt Systems

MW PEM Electrolyzer

Laboratory test stations

Catalysts

Stack components

Coatings

Analytics and in-situ diagnostics
Evaluation of catalysts and coatings

Rotating ring disc electrode (RRDE)

Sample holder for corrosion measurements (1 cm² exposed area)

6 Cell - 120 cm² – stack (E92 model)

4 Cell - 25 cm² - stack

0.75 - 2.5 Nm³ H₂ h⁻¹ “Hylyzer” PEM electrolyzer unit, 8 bar

6 Cell - 120 cm² – stack (E92 model)
Designing a cost effective, active and durable electro-catalyst for OER

- **Ir** as active and stable metal center for OER

- Enhancement of activity of Ir by adding A. Reduction of Ir content

- Enhancement of durability of Ir by adding B (PMG metal) / HOR (less H₂ crossover)

- Increase of electrochemical surface area (ECSA), activity and durability by using an electro-ceramic support MO₂-δ. Cost reduction

**Challenge**: Develop a highly active and stable OER catalyst than can be mass-produced at a reduced cost

Target material: \( \text{A}_x\text{Ir}_y\text{B}_z/\text{MO}_2-\delta \)
Synthesis of oxygen evolution reaction (OER) catalysts

**IrOₓ-Ir**<sup>a</sup>, **Ir<sub>0.7</sub>Ru<sub>0.3</sub>O<sub>2</sub>**<sup>b</sup>

**Ir precursor**

**IrCl₃** (0.0749 g) → ANH ethanol (50 ml) → Ultrasonic

**Reducing agent**

**NaBH₄** (0.114 g) → ANH ethanol (80 ml) → Ultrasonic

**Mixing solution**

(4 h, 800 rpm, Ar- atmosphere)

**Addition of reducing agent to mixing solution**

(4 h, 800 rpm, Ar- atmosphere)

**Cleaning of Ir/Ti₄O₇ catalyst**

(several times with DI H₂O and ethanol)

**Ir/Ti₄O₇**<sup>c</sup>, **Ir/SnO₂:Sb-Aerogel**<sup>d</sup>

**Ti₄O₇ support (Changsha PuRong)**

**CTAB** (1.17 g) → ANH ethanol (120 ml) → Ultrasonic

**Ti₄O₇** (0.113 g) → ANH ethanol (80 ml) → Ultrasonic

- Enviromentally friendly synthesis
- Scalable for large production: 1 g d⁻¹
- Estimated cost < 100 € g⁻¹

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Patent DE 102015101249 A1
Electrochemically oxidized IrO$_x$-Ir nanoparticles

- Metallic Ir nanoparticles (agglomerated) with large number of defects
- Almost identical structure, morphology and surface properties than Ir-black
- 5-fold higher OER activity than Ir-black
- Negligible $E_{\text{cell}}$ increase after more than 100 h in PEM electrolyzer at 2 A cm$^{-2}$, 80°C

Ir/SnO$_2$:Sb-Aerogel: Morphology and surface properties

- Metallic Ir deposited on three-dimensional (3D) aerogel SnO$_2$:Sb (ARMINES)

- NH$_4$VO$_3$ added to IrCl$_3$ solution: Ir/SnO$_2$:Sb-mod-V

- Cl impurities are 5 times higher in the case of Ir/SnO$_2$:Sb

- VO$_2$ or V$_2$O$_5$ allows retaining the aerogel structure under atmospheric drying

**Ir/SnO$_2$:Sb-Aerogel: Electrochemical activity**

- **OER activities:** Ir/SnO$_2$:Sb (94.6 $\text{A g}^{-1}$) and Ir/SnO$_2$:Sb-mod-V (121.5 $\text{A g}^{-1}$)

- The slight difference in Tafel slopes attributed to the influence from MMOSI:
  

- Ir/SnO$_2$:Sb-mod-V allows decreasing of more than 70 wt.% for precious metal

- Cu-UPD enables the calculation of ECSA

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**Does V addition play an active role in electrocatalysis?**

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**Ir/SnO₂:Sb-Aerogel: Electrochemical stability**

- RDE stability tests based on a protocol developed by P. Strasser and co-workers:
  

- After test V wt% decreases one order of magnitude

- Sb and Ir practically remained unchanged
  - Ir dissolution?
  - Decrease of electronic conductivity of SnO₂:Sb?

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Near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) allows monitoring of the surface state of MEAs with RuO$_2$ and Ir$_{0.7}$Ru$_{0.3}$O$_2$ during OER.

- Ir protects Ru from the formation of unstable hydrous Ru$^{IV}$ oxide.
- OER occurs through a surface Ru$^{VIII}$ intermediate.

Summary

• Cost-effective and environmentally friendly synthesis of anode catalysts for PEM electrolyzers

• 5-fold higher activity of IrO$_x$-Ir vs. Ir-black. The enhancement is attributed to the ligand effect and low coordinate sites

• The use of SnO$_2$:Sb-Aerogel allows decreasing more than 70 wt.% of Ir in the catalyst layer and improves stability

• New mechanisms of stability and OER for Ir$_{0.7}$Ru$_{0.3}$O$_2$ uncovered by near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS)

• In operando advanced spectroscopy techniques are necessary to understand the reaction and degradation mechanism of PEM electrolyzer catalysts
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