Synthesis of Highly Active Iridium Catalysts for Anodes of Proton Exchange Membrane Electrolyzers

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Contents

• Hydrogen as energy vector

• Cost and availability of iridium catalyst

• Oxygen evolution reaction (OER) catalyst design

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

• Physical characterization, 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 renewable energy (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. Mobilility 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

\[ E_{\text{cell}} = 2 \text{ V}, \ p\text{H} = 0, \ 80 \ ^\circ \text{C} \]
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 \(\text{H}_2\)


PEM electrolysis technology is not scalable to the TW level!
DLR activities in PEM Electrolysis: from Fundamentals to Megawatt Systems

- Catalysts
- Coatings
- Stack components
- MW PEM Electrolyzer
- Laboratory test stations
- Analytics and in-situ diagnostics
Designing a cost effective, active and durable electro-catalyst for oxygen evolution reaction (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) / hydrogen oxidation reaction (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: AₓIrᵧB₂/MO₂⁻δ
Synthesis of oxygen evolution reaction (OER) catalysts

\[ \text{IrO}_x - \text{Ir}^a, \text{Ir}_{0.7}\text{Ru}_{0.3}\text{O}_x^b \]

\[ \text{IrCl}_3 (0.0749 \text{ g}) \rightarrow \text{ANH ethanol (50 ml)} \rightarrow \text{Ultrasound} \]

\[ \text{Reducing agent} \]

\[ \text{NaBH}_4 (0.114 \text{ g}) \rightarrow \text{ANH ethanol (80 ml)} \rightarrow \text{Ultrasound} \]

\[ \text{NaBH}_4 + \text{IrCl}_3 \cdot x\text{H}_2\text{O} \rightarrow \]
\[ \text{Ir}^0 + \text{H}_3\text{BO}_3 + \text{NaCl} + \text{HCl} + y\text{IrCl}_3 + \text{H}_2 \]

\[ \text{Mixing solution (4 h, 800 rpm, Ar- atmosphere)} \]

\[ \text{Ir}/\text{Ti}_4\text{O}_7^c, \text{Ir}/\text{SnO}_2:\text{Sb-Aerogel}^d \]

\[ \text{Ti}_4\text{O}_7 \text{ support (Changsha PuRong)} \]

\[ \text{ANH ethanol (120 ml)} \rightarrow \text{Ultrasound} \]

\[ \text{CTAB (1.17 g)} \]

\[ \text{ANH ethanol (120 ml)} \rightarrow \text{Ultrasound} \]

\[ \text{Ti}_4\text{O}_7 (0.113 \text{ g}) \]

- Environmentally friendly synthesis
- Scalable for large production: 1 g d\(^{-1}\)
- Estimated cost < 100 € g\(^{-1}\)

\[ ^a \text{Lettenmeier et al. Angew. Chemie 2016, 128, 752–756.} \]

\[ ^b \text{Wang et al. Nano Energy, 2017, 34, 385–391.} \]

\[ ^c \text{Wang et al. Phys. Chem. Chem. Phys. 2016, 18, 4487–4495.} \]


Patent pending DE 102015101249 A1
Electrochemically oxidized $\text{IrO}_x$-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 A g$^{-1}$) and Ir/SnO$_2$:Sb-mod-V (121.5 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


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

The resulting material shows 13-fold higher activity compared to the state-of-the-art Ir$_{0.7}$Ru$_{0.3}$O$_2$.

MEA test in PEM electrolyzer confirmed the high performance and stability (>400 h) of the Ru-leached Ir anode.

Surface O$^-$ formation and surface hydroxyls formation are plausible explanations for a superior activity.

\[\text{Electrochemical leaching of Ru from metallic Ir}_{0.7}\text{Ru}_{0.3}\]

\[\text{STEM}\quad \text{XPS}\]

\[\text{RDE}\quad \text{PEM electrolyzer}\]

Stabilization mechanism of Ru in $\text{Ir}_{0.7}\text{Ru}_{0.3}\text{O}_2$

- Near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) allows monitoring of the surface state of MEAs with RuO$_2$ and $\text{Ir}_{0.7}\text{Ru}_{0.3}\text{O}_2$ (rutile) during OER
- Ir protects Ru from the formation 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 $\text{IrO}_x$-Ir vs. Ir-black. The enhancement is attributed to the ligand effect and low coordinate sites

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

• Electrochemical leaching of Ru from metallic $\text{Ir}_{0.7}\text{Ru}_{0.3}$ leads to 13-fold higher activity compared to the state-of-the-art $\text{Ir}_{0.7}\text{Ru}_{0.3}\text{O}_2$

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

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