20th Topical Meeting
of the International Society of Electrochemistry
Advances in Lithium and Hydrogen Electrochemical Systems for Energy Conversion and Storage

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

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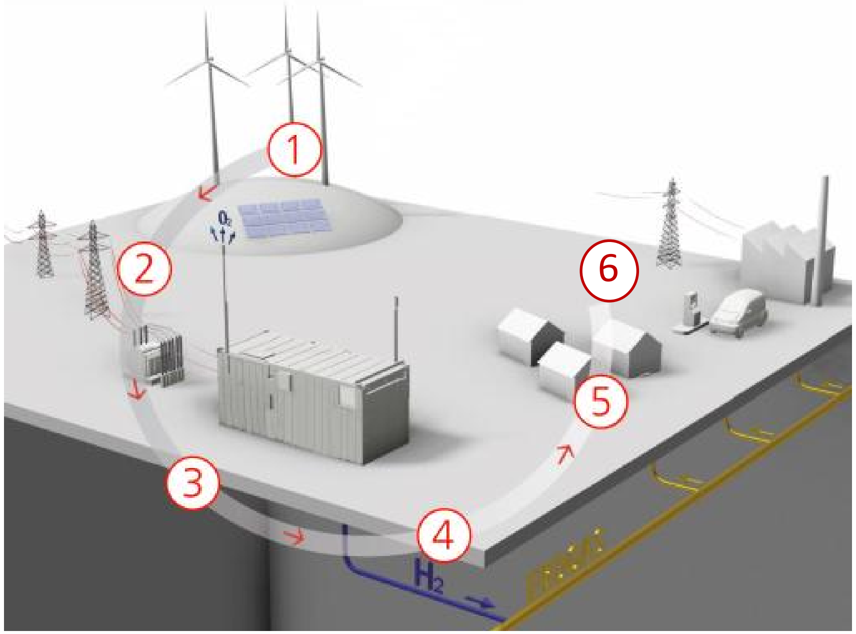
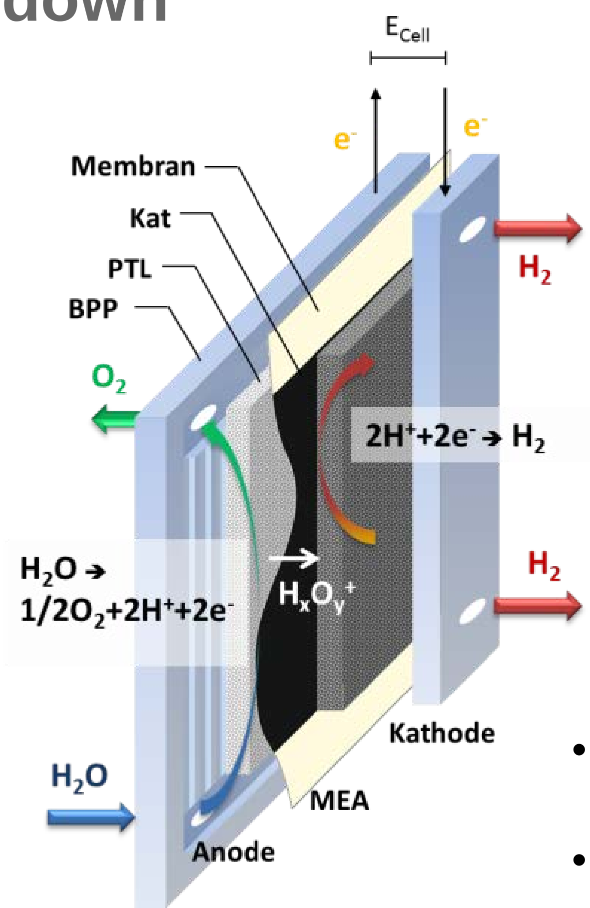
Hydrogen as energy vector

- High percentage of renewable energy in energy supply chain need long-term storage facilities
- Intermittend oversupply of renewable energy (RE) will increase significantly (in 2050 ~25 TWh) will be available for hydrogen production in Germany

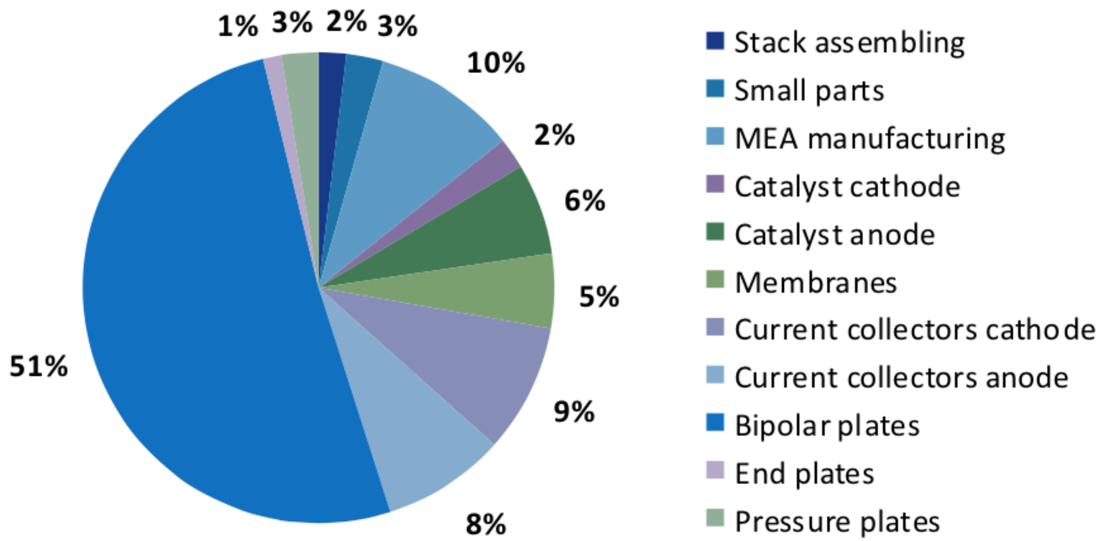


1. Intermittent oversupply of RE from wind and sun
2. Feeding in electrical grid
3. Hydrogen production via electrolysis (3000-4000 hours per year)
4. Hydrogen can be distributed via the natural gas grid
5. Hydrogen can be used in industry and for heat production
6. Mobilily for fuel cell-driven vehicles

PEM electrolysis: Working principle and cost break down



E_{cell}= 2 V, pH = 0, 80 °C

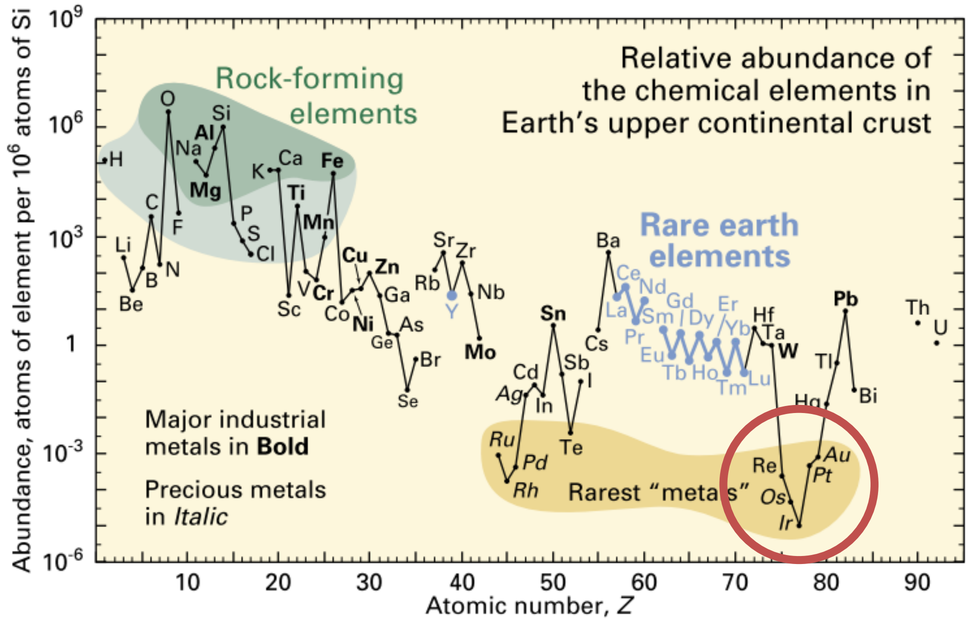


Study on development of water electrolysis in the EU.
Final Report. E4tech Fuel Cells and Hydrogen Joint Undertaking; 2014

- Bipolar plates are the most expensive component (51%) of the stack
- Currently the cost 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 H_2 regulations

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 $mg_{iridium}$ cm^{-2}
  Cathode: < 1 $mg_{platinum}$ cm^{-2}
- 7530 tons of Ir are required for PEM electrolyzers operating at E_{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



Haxel *er al.* Mineral, O. U. R. United States Geol. Surv. Fact Sheet 2002, 87, 4.

PEM electrolysis technology is not scalable to the TW level!

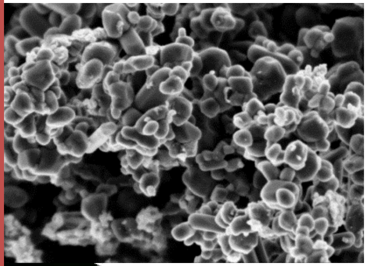
Vesborg *et al.* RSC Adv. **2012**, 2 (21), 7933.
Paoli, E. A. *et al.* Chem. Sci. **2015**, 6 (1), 190.

DLR activities in PEM Electrolysis: from Fundamentals to Megawatt Systems

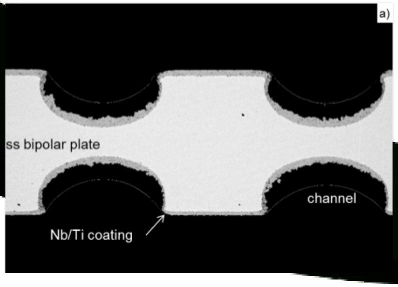
MW PEM Electrolyzer

Laboratory test stations

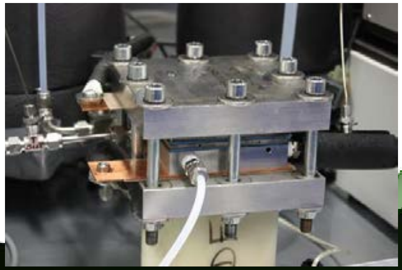
Catalysts



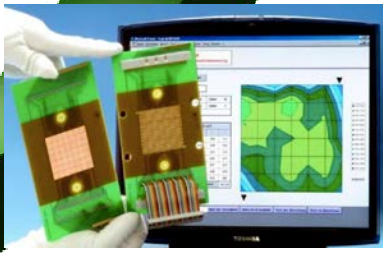
Coatings



Stack components



Analytics and in-situ diagnostics



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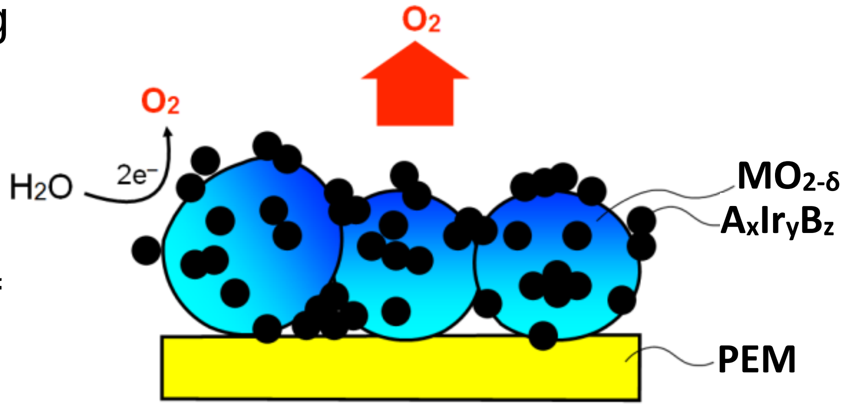
Designing a cost effective, active and durable electro-catalyst for oxygen evolution reaction (OER)

- **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 H_2 crossover)
- Increase of electrochemical surface area (ECSA), activity and durability by using an electro-ceramic support $MO_{2-\delta}$. Cost reduction

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

Target material: $\mathbf{A_xIr_yB_z/MO_{2-\delta}}$



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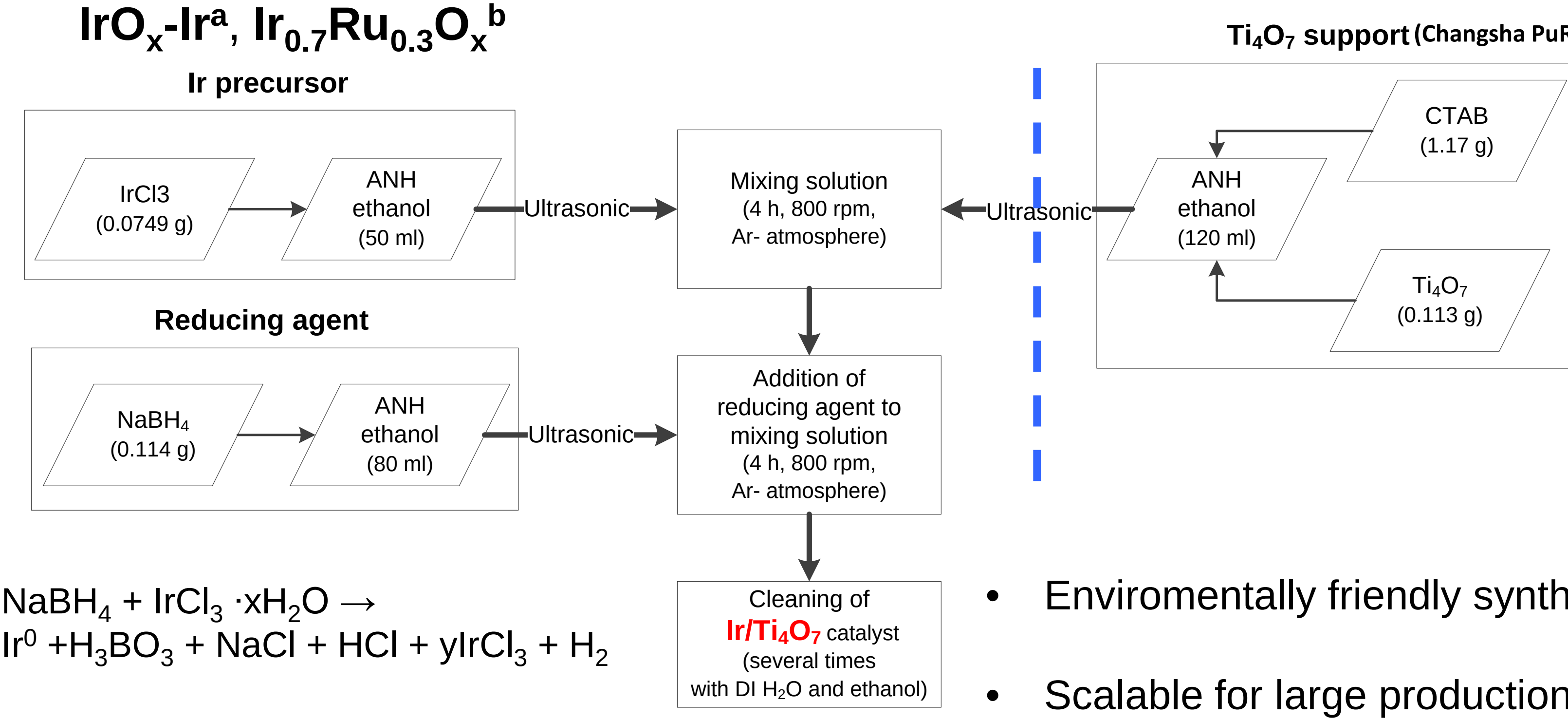
Synthesis of oxygen evolution reaction (OER) catalysts

IrO_x-Ir[a], $Ir_{0.7}Ru_{0.3}O_x$[b]

Ir/Ti_4O_7[c], **Ir/SnO_2:Sb-Aerogel[d]**



$$NaBH_4 + IrCl_3 \cdot xH_2O \rightarrow$$
$$Ir^0 + H_3BO_3 + NaCl + HCl + yIrCl_3 + H_2$$

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

[a]Lettenmeier *et al.* Angew. Chemie **2016**, *128*, 752–756.
[b]Wang et al. Nano Energy, **2017**, 34, 385–391.
[c]Wang *et al.* Phys. Chem. Chem. Phys. **2016**, *18*, 4487–4495.
[d]Wang *et al.* J. Mater. Chem. A, **2017**, 5, 3172–3178.

Patent pending DE 102015101249 A1

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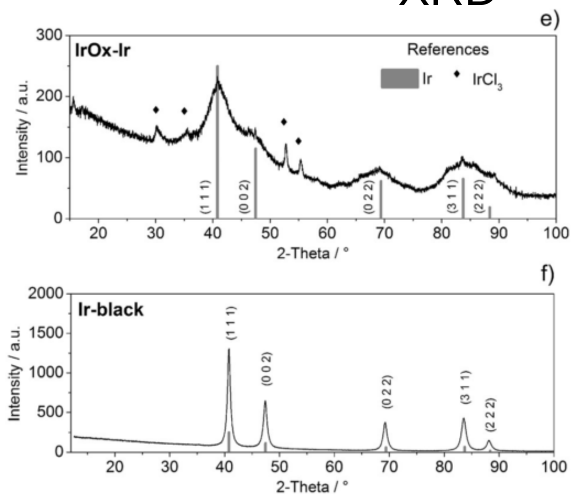
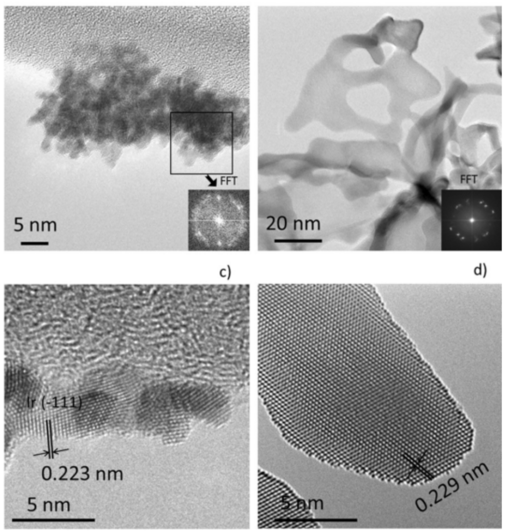
Electrochemically oxidized IrO_x-Ir nanoparticles

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

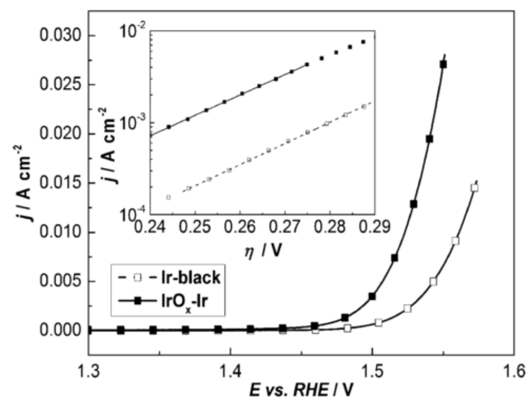
XRD

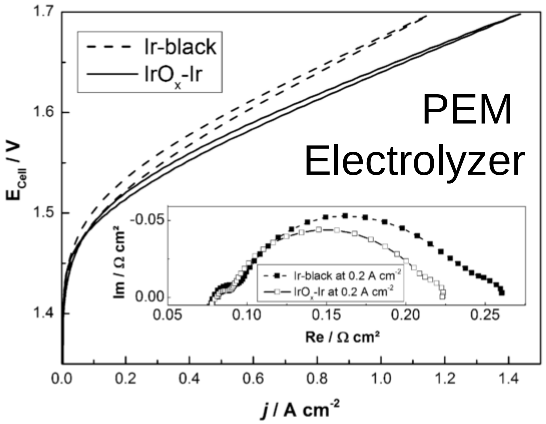


TEM



RDE



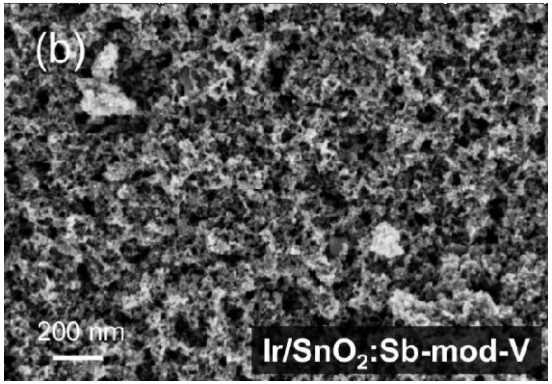


Lettenmeier *et al.* Angew. Chemie **2016**, *128*, 752–756.

Ir/SnO_2:Sb-Aerogel: Morphology and surface properties

- Metallic Ir deposited on three-dimensional (3D) aerogel SnO_2:Sb (ARMINES)
- NH_4VO_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_2O_5 allows retaining the aerogel structure under atmospheric drying

SEM



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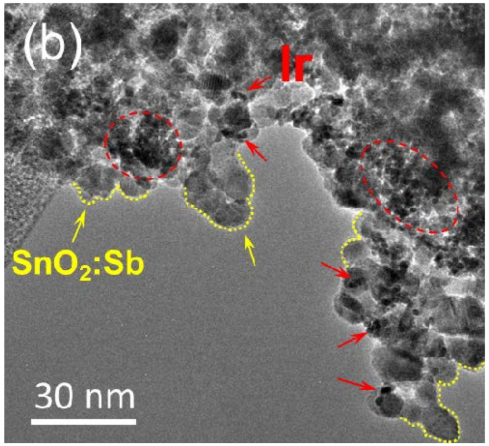
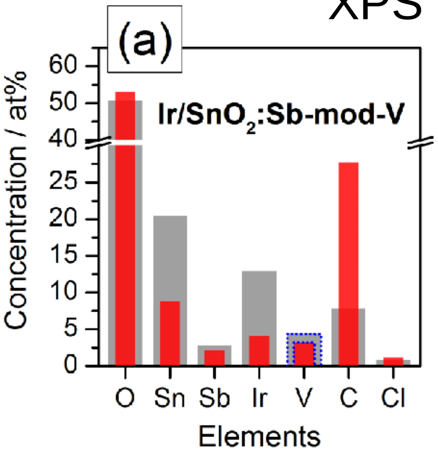
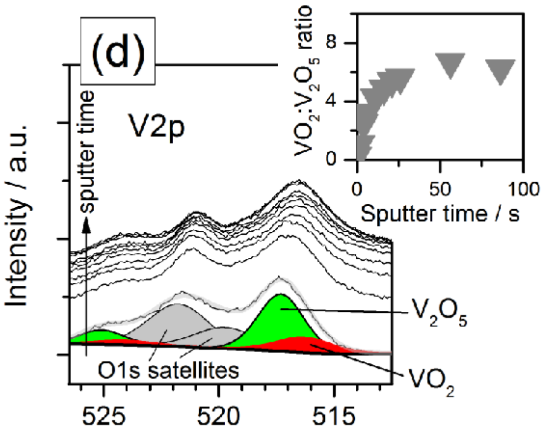


XPS





Wang *et al.* J. Mater. Chem. A, **2017**, 5, 3172–3178.

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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})

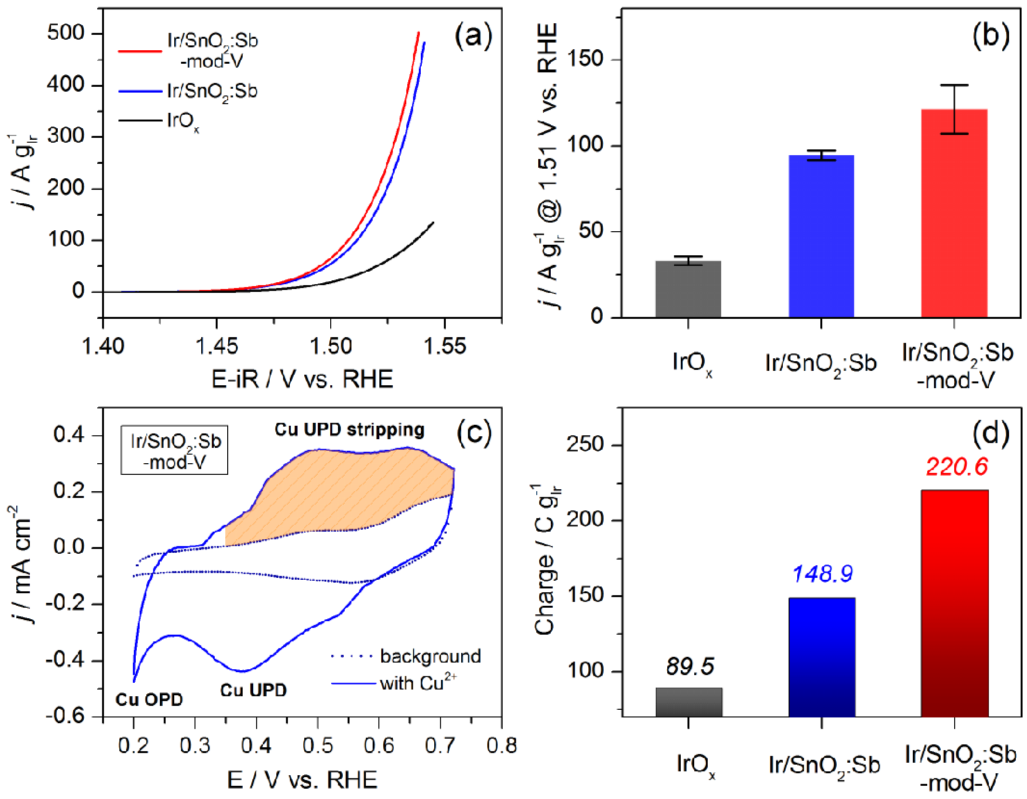
- The slight difference in Tafel slopes attributed to the influence from MMOSI:

  H. S. Oh *et al.* P. Strasser, *J. Am. Chem. Soc.*, **2016**, 138, 12552-12563.

- Ir/SnO_2:Sb-mod-V allows decreasing of more than 70 wt.% for precious metal

- Cu-UPD enables the calculation of ECSA

  Wang *et al.* J. Mater. Chem. A, **2017**, 5, 3172–3178.

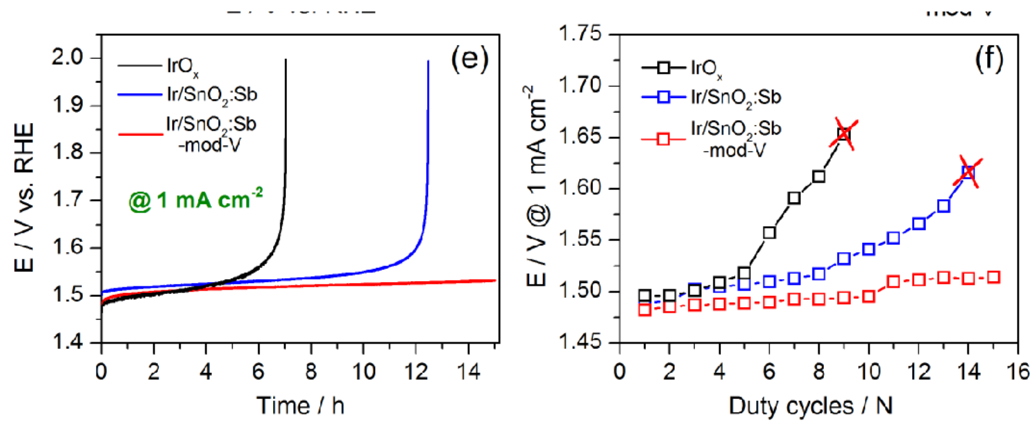


Does V addition play an active role in electrocatalysis?

Ir/SnO_2:Sb-Aerogel: Electrochemical stability

- RDE stability tests based on a protocol developed by P. Strasser and co-workers:
  Nong, H. N. et al. Angew. Chemie **2015**, 54 (10), 2975.
- After test V wt% decreases one order of magnitude
- Sb and Ir pratically remained unchanged
  - Ir dissolution?
  - Decrease of electronic conductivity of SnO_2:Sb?

Wang *et al.* J. Mater. Chem. A, **2017**, 5, 3172–3178.



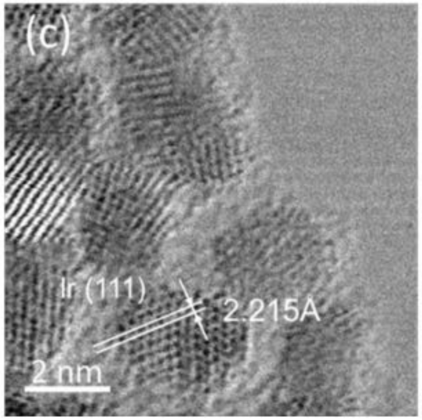
Ir/SnO_2:Sb-mod-V: fresh electrode										
Analyzed Areas	C / wt.%	O / wt.%	F / wt.%	Na / wt.%	Cl / wt.%	V / wt.%	Sn / wt.%	Sb / wt.%	Ir / wt.%	Au / wt.%
A1	6.83	9.8	7.16	1.19	0.39	3.15	29.68	3.81	17.74	20.26
A2	6.84	9.95	6.1	0.96	0.34	2.74	27.8	3.66	17.34	24.27
A3	7.3	10.14	6.08	1.14	0.39	2.71	28.13	3.51	17.4	23.21

Ir/SnO_2:Sb-mod-V: operated electrode										
Analyzed Areas	C / wt.%	O / wt.%	F / wt.%	Na / wt.%	Cl / wt.%	V / wt.%	Sn / wt.%	Sb / wt.%	Ir / wt.%	Au / wt.%
A1	7.07	13.32	5.95	N/A	0.39	0.33	29.82	3.2	18.79	21.12
A2	7.36	13.68	6.93	N/A	0.28	0.23	28.43	2.95	17.14	23
A3	7.52	13.51	6.18	N/A	0.4	0.32	27.73	3.3	18.57	22.47

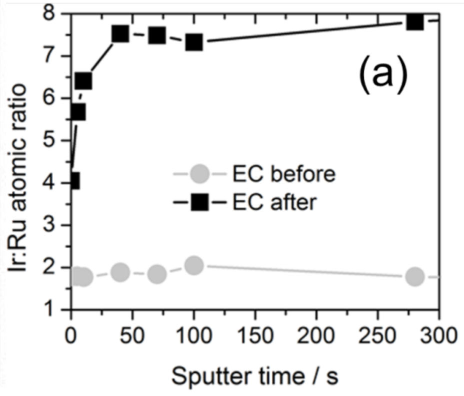
Electrochemical leaching of Ru from metallic $Ir_{0.7}Ru_{0.3}$

- 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^{I-} formation and surface hydroxyls formation are plausible explanations for a superior activity

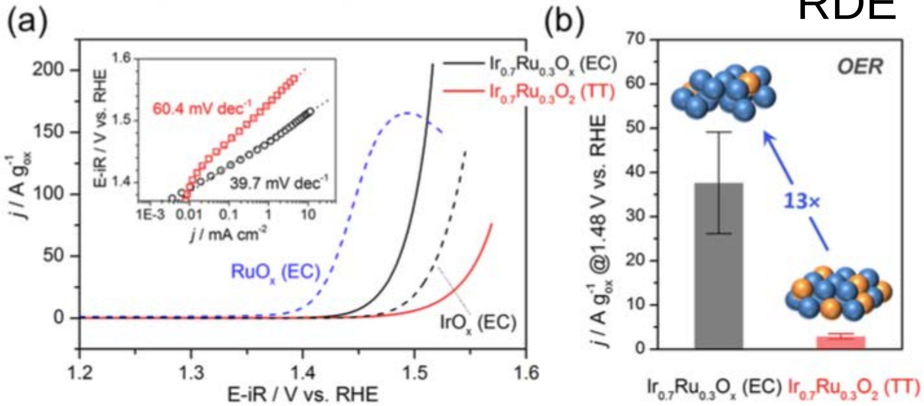
STEM



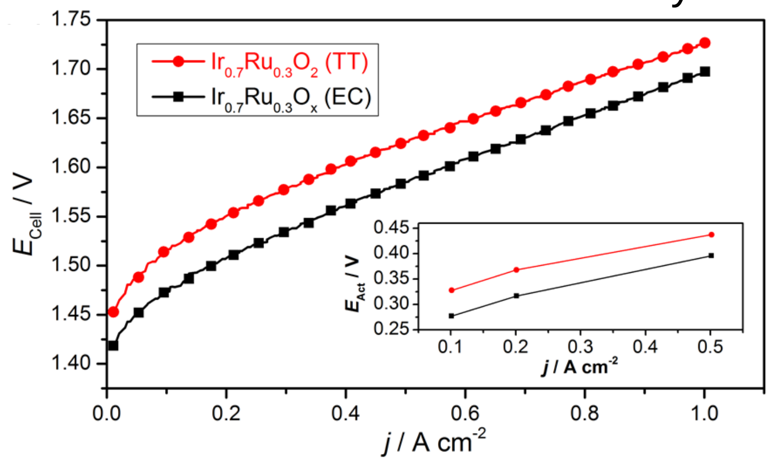
XPS



RDE



PEM electrolyzer



[b]Wang et al. Nano Energy, **2017**, 34, 385–391.

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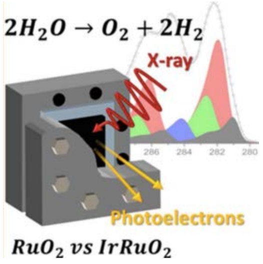
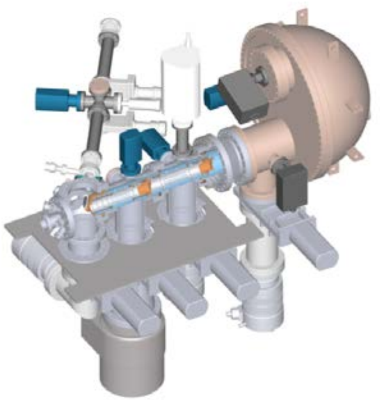
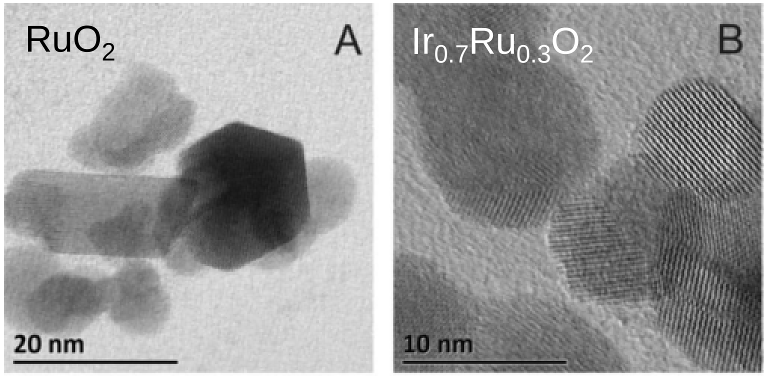
NAP-XPS set-up at BESSY II

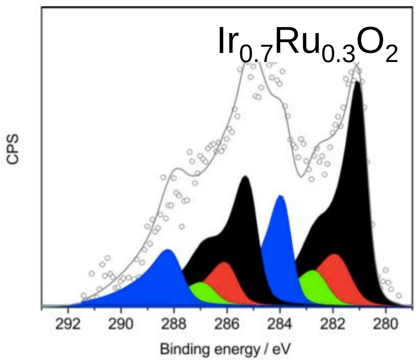
Stabilization mechanism of Ru in $Ir_{0.7}Ru_{0.3}O_2$

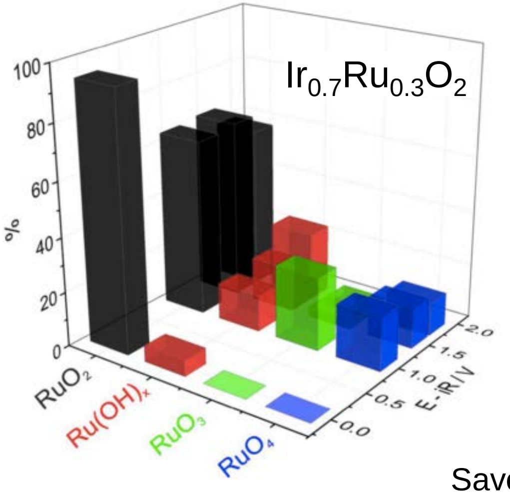
- Near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) allows monitoring of the surface state of MEAs swith RuO_2 and $Ir_{0.7}Ru_{0.3}O_2$ (rutile) during OER
- Ir protects Ru from the formation unstable hydrous Ru^{IV} oxide
- OER occurs through a surface Ru^{VIII} intermediate

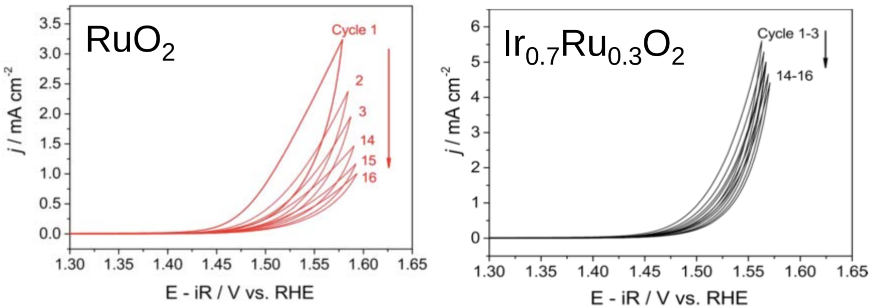












Saveleva *et al.* J. Phys. Chem. Lett., **2016**, *7*, 3240–3245

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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
- Electrochemical **leaching of Ru** from metallic $Ir_{0.7}Ru_{0.3}$ leads to 13-fold higher activity compared to the state-of-the-art $Ir_{0.7}Ru_{0.3}O_2$
- 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 operado advanced spectroscopy techniques are necessary to understand the reaction and degradation mechnism of PEM electrolyzer catalysts

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