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 IrO_x-Ir, Ir/SnO_2:Sb-aerogel, $Ir_{0.7}Ru_{0.3}O_2$ catalysts
- OER activity and stability
- Summary

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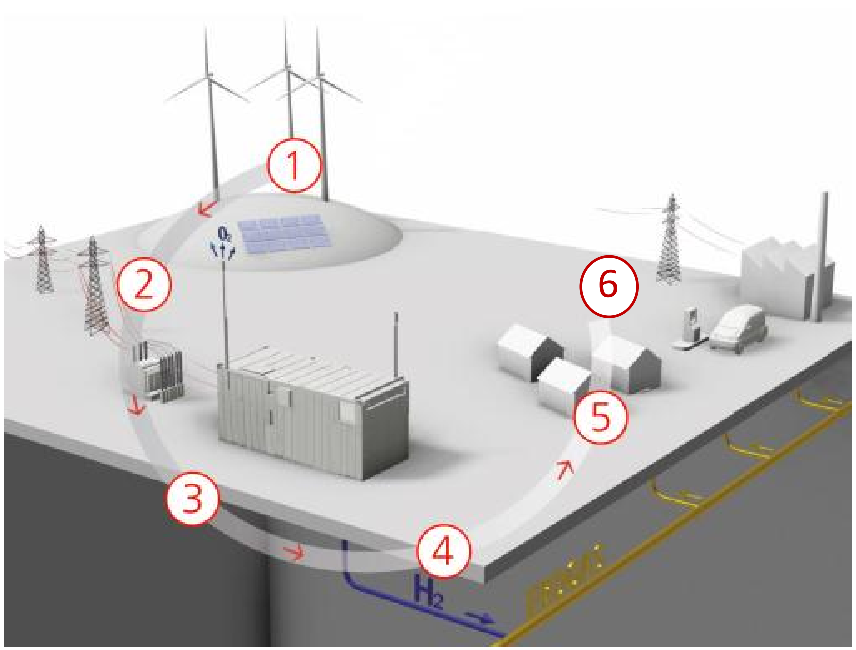
Hydrogen as energy vector

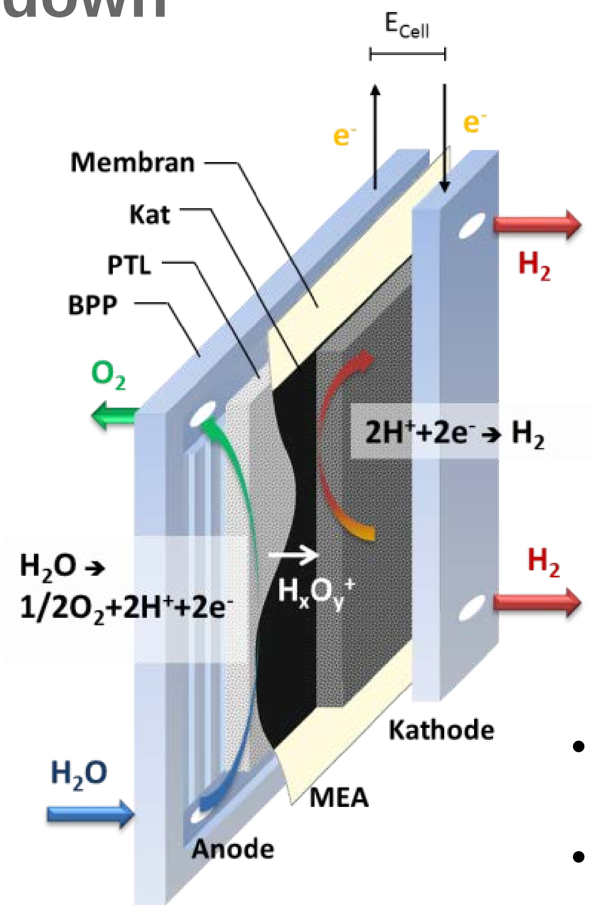
- High percentage of renewable energy in energy supply chain need long-term storage facilities

- Intermittend oversupply of RE will increase significantly (in 2050 ~25 TWh will be available for hydrogen production in Germany

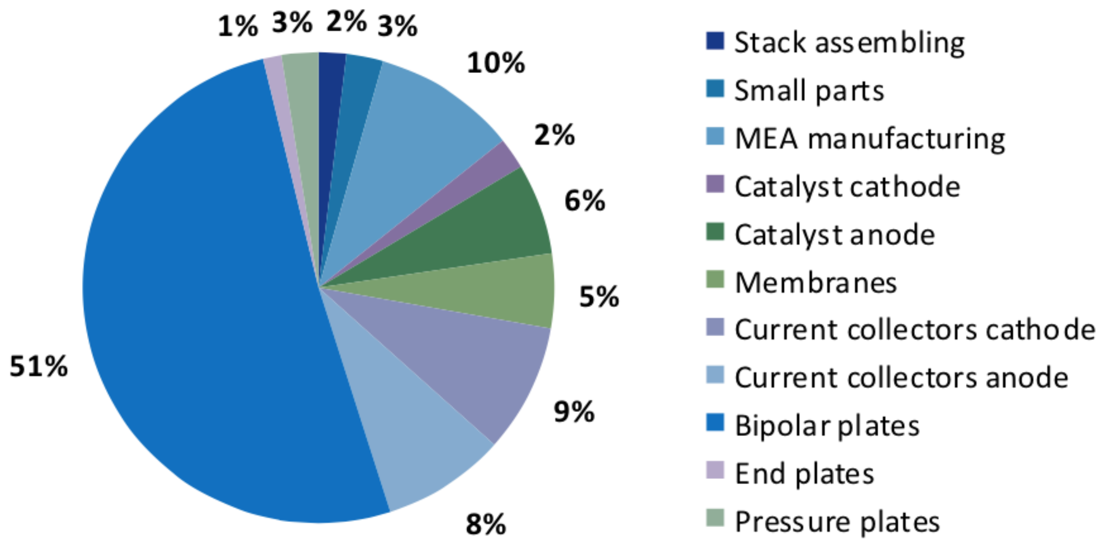


1. Intermittent oversupply of RE from wind and sun
2. Feeding in electrical grid
3. Hydrogen production via electrolysis (3000-4000 hours per year)
4. Hydrogen can be distributed via the natural gas grid
5. Hydrogen can be used in industry and for heat production
6. Mobilily for fuel cell-driven vehicles

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

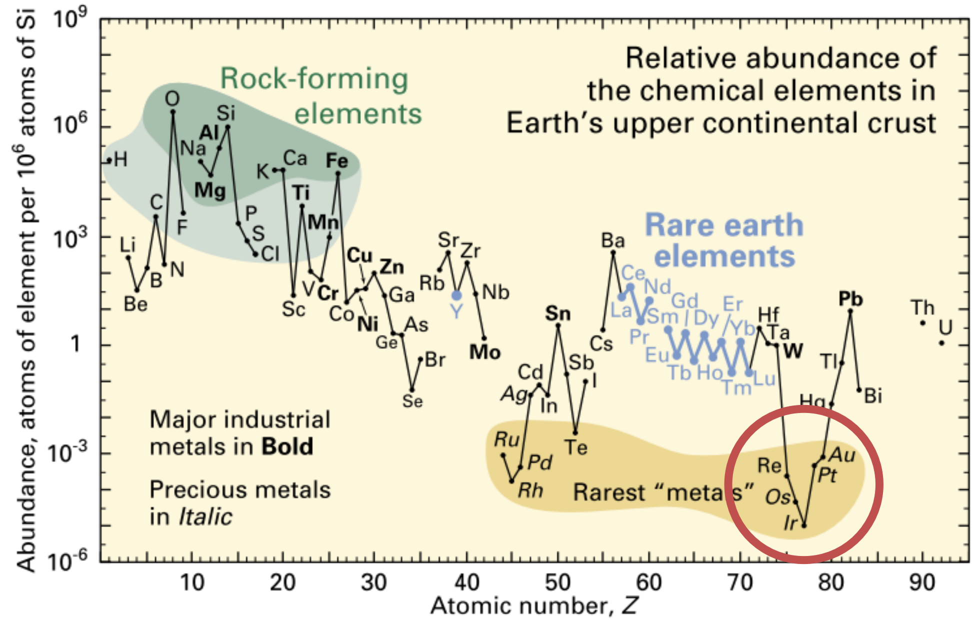
Cost and availability of PEM electrolyzer catalysts

- 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!

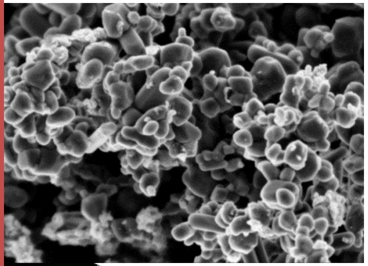
Vesborg *et al.* RSC Adv. **2012**, 2 (21), 7933.
Paoli, E. A. *et al.* Chem. Sci. **2015**, 6 (1), 190.

DLR activities in PEM Electrolysis: from Fundamentals to Megawatt Systems

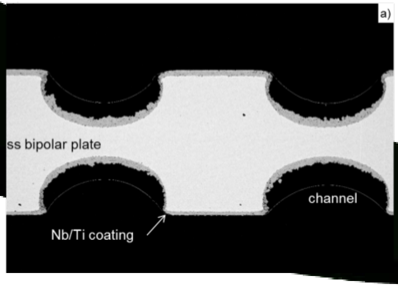
MW PEM Electrolyzer

Laboratory test stations

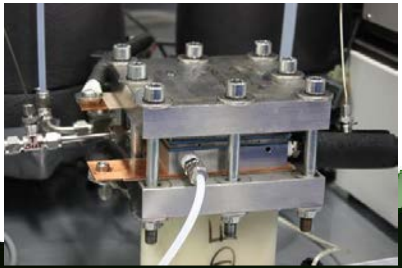
Catalysts



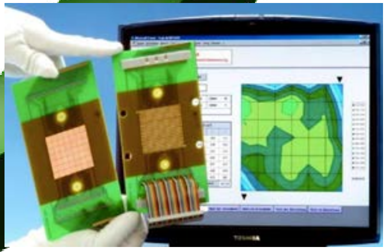
Coatings



Stack components



Analytics and in-situ diagnostics



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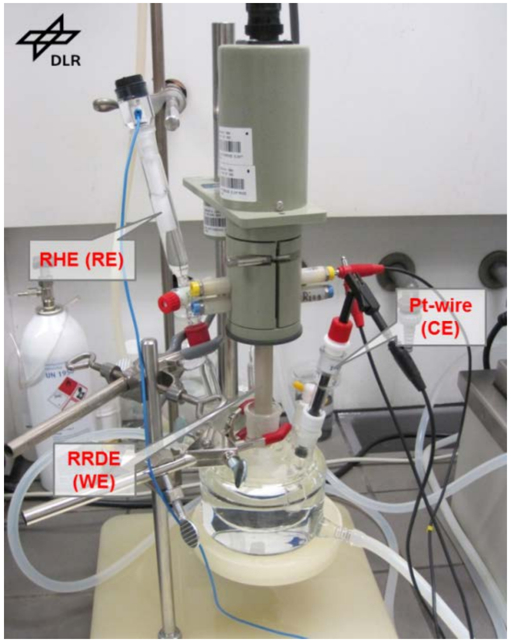
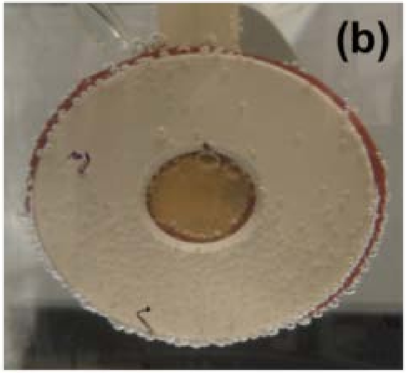
Evaluation of catalysts and coatings

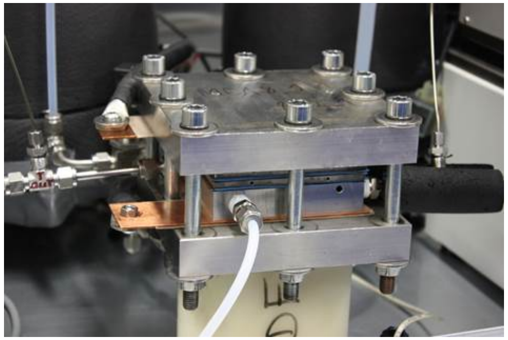
Rotating ring disc electrode (RRDE)



Sample holder for corrosion measurements (1 cm^2 exposed area)



4 Cell - 25 cm^2 - stack



HYDROGENICS
Advanced Hydrogen Solutions

6 Cell - 120 cm^2 – stack (E92 model)

0.75 - 2.5 Nm^3 H_2 h^{-1} “Hylyzer” PEM electrolyzer unit, 8 bar

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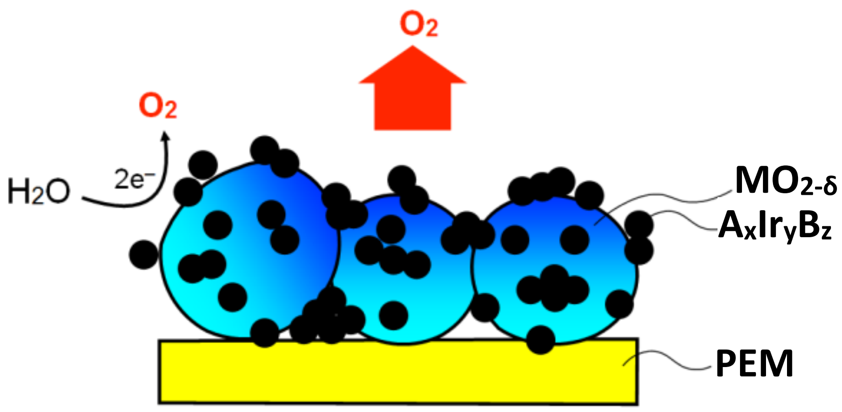
Designing a cost effective, active and durable electro-catalyst for OER

- **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 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

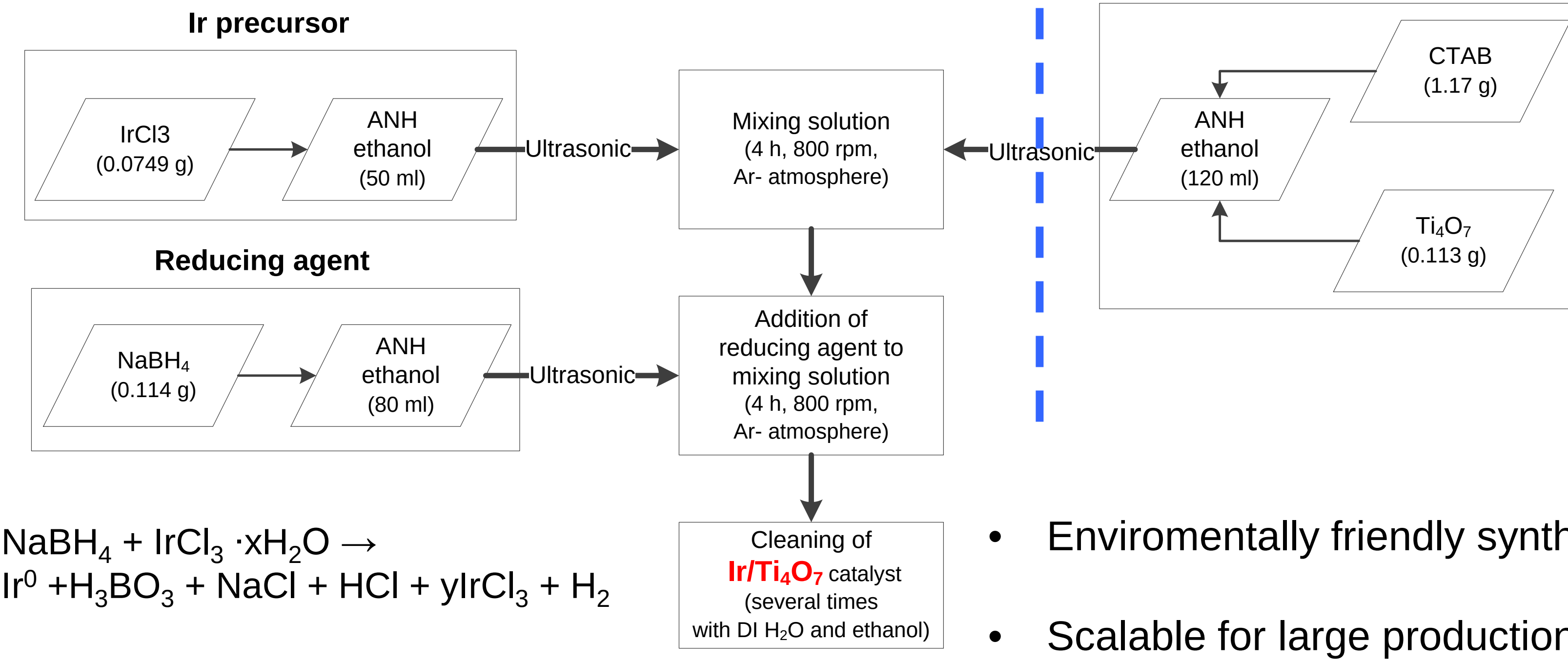
Target material: $\mathbf{A_xIr_yB_z/MO_{2-\delta}}$



Synthesis of oxygen evolution reaction (OER) catalysts

IrO_x-Ir[a], $Ir_{0.7}Ru_{0.3}O_2$[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]Saveleva et al. J. Phys. Chem. Lett. **2016**, *7*, 3240–3245.

[c]Wang *et al.* Phys. Chem. Chem. Phys. **2016**, *18*, 4487–4495.

[d]Wang *et al.* J. Mater. Chem. A, **2017**, *in press.*

Patent DE 102015101249 A1

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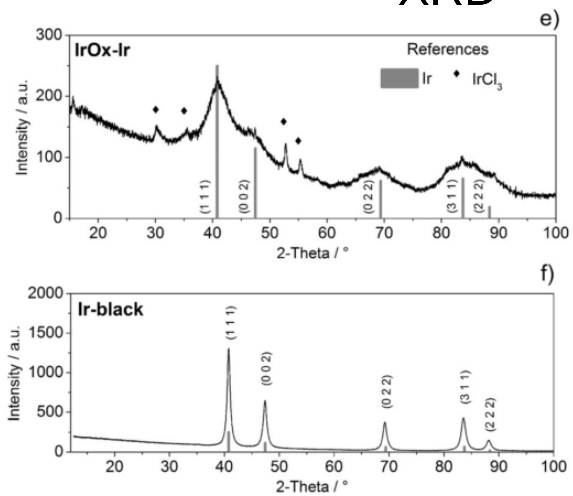
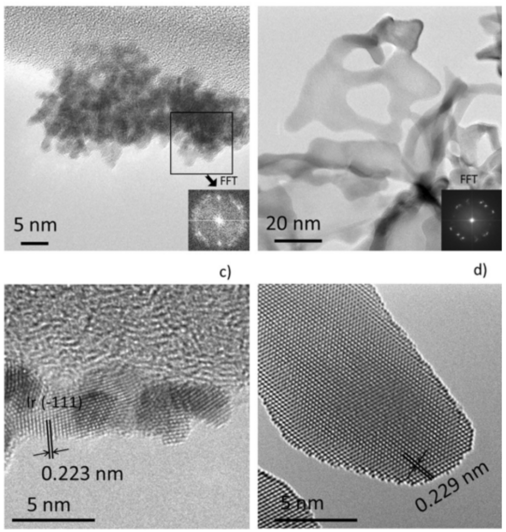
Electrochemically oxidized IrO_x-Ir nanoparticles

- 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

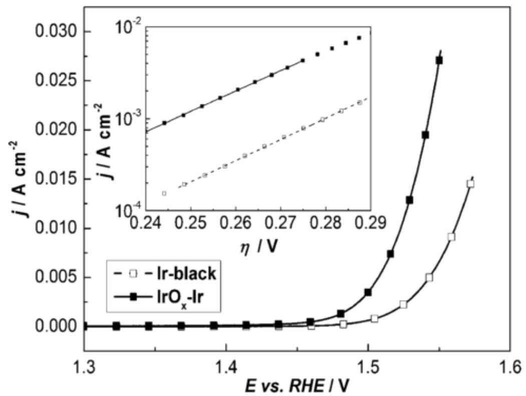
XRD

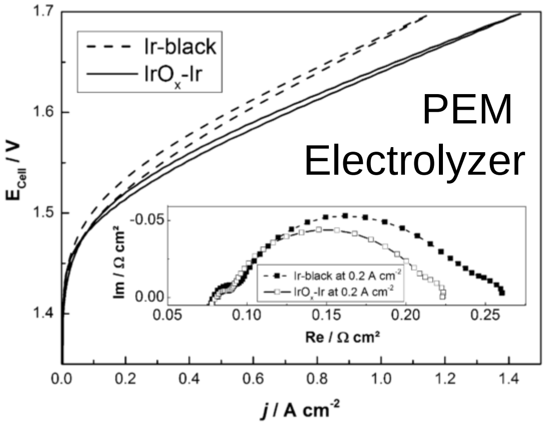


TEM



RDE



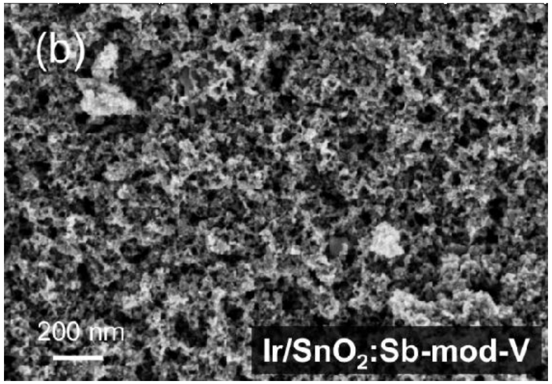


Lettenmeier *et al.* Angew. Chemie **2016**, *128*, 752–756.

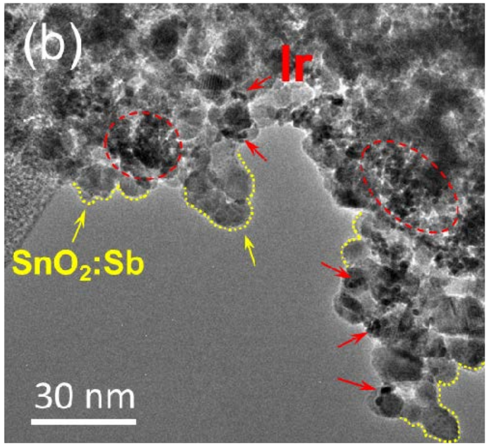
Ir/SnO_2:Sb-Aerogel: Morphology and surface properties

- 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

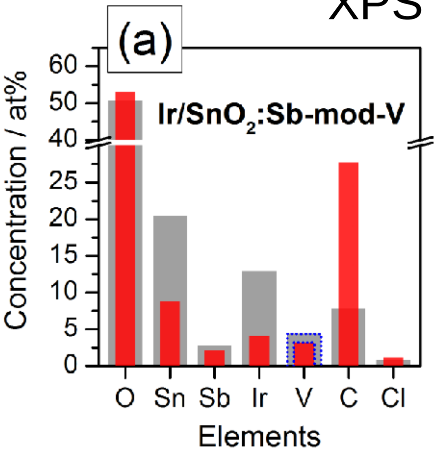
SEM

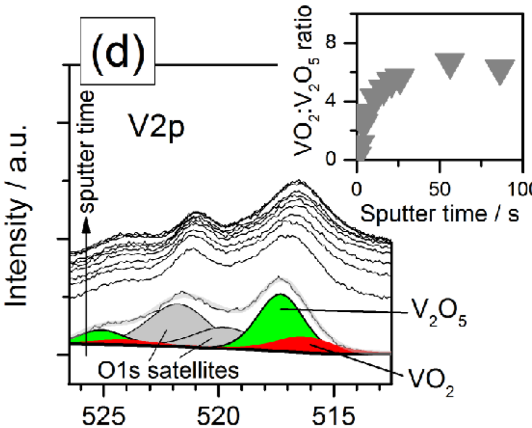


TEM



XPS





Wang *et al.* J. Mater. Chem. A, **2017**, *in press.*

DLR ARMINES

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})

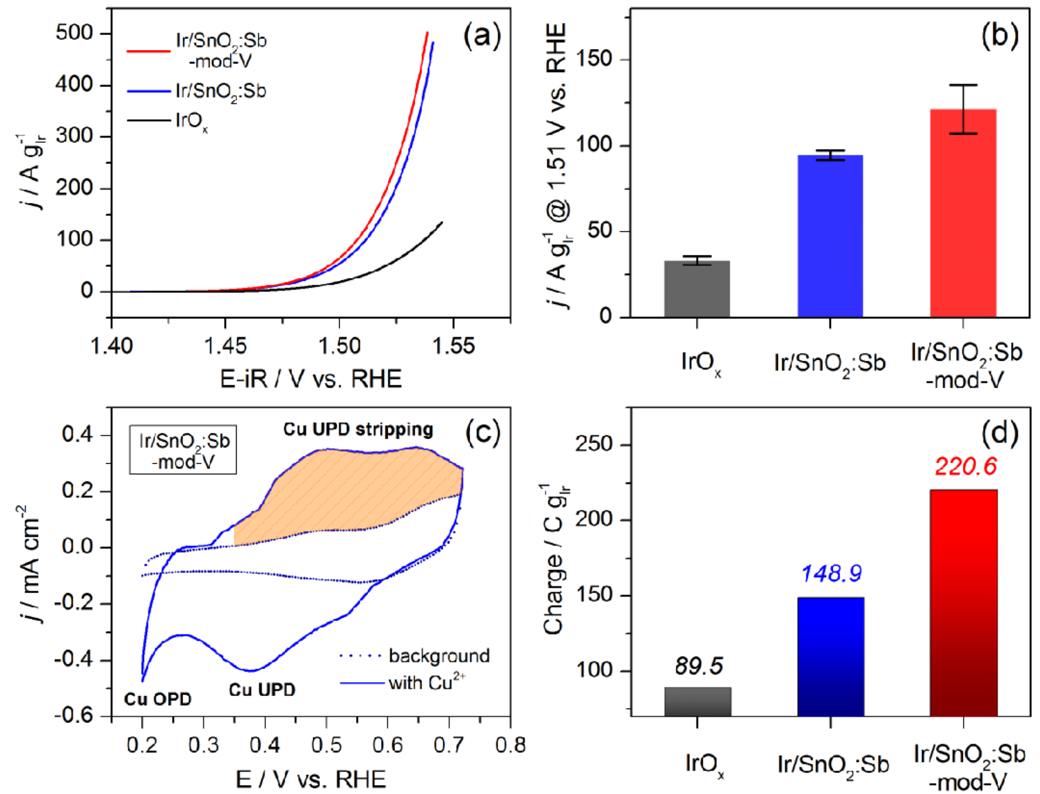
- The slight difference in Tafel slopes attributed to the influence from MMOSI:

  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

  [d]Wang *et al.* J. Mater. Chem. A, **2017**, *in press.*



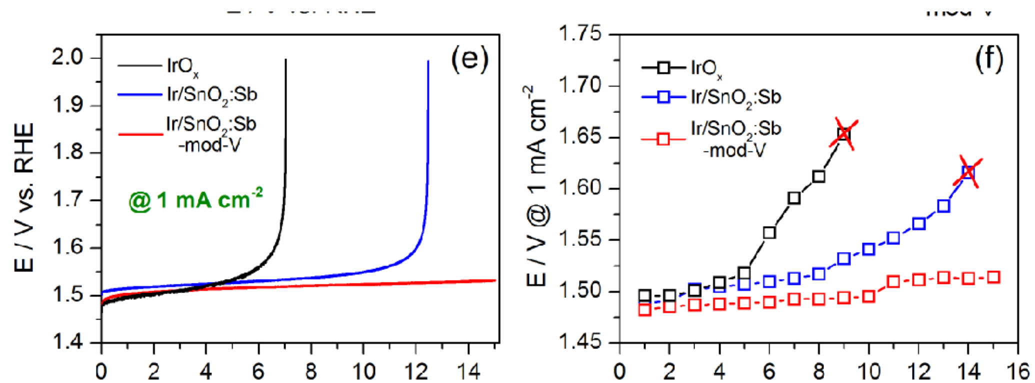
Does V addition play an active role in electrocatalysis?

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?



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

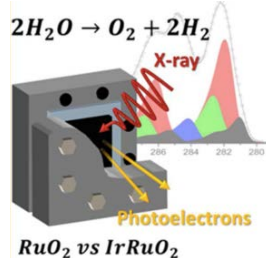
Ir/SnO_2:Sb-mod-V: operated electrode										
Analyzed Areas	C / wt.%	O / wt.%	F / wt.%	Na / wt.%	Cl / wt.%	**V / wt.%**	Sn / wt.%	Sb / wt.%	Ir / wt.%	Au / wt.%
A1	7.07	13.32	5.95	N/A	0.39	**0.33**	29.82	3.2	18.79	21.12
A2	7.36	13.68	6.93	N/A	0.28	**0.23**	28.43	2.95	17.14	23
A3	7.52	13.51	6.18	N/A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

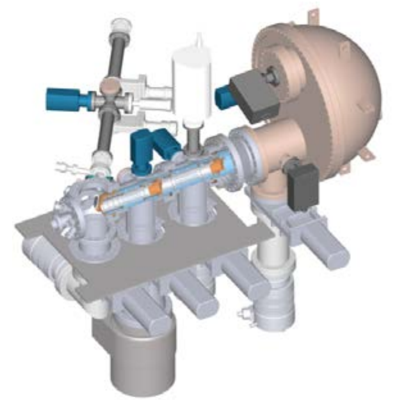
[d]Wang *et al.* J. Mater. Chem. A, **2017**, *in press.*

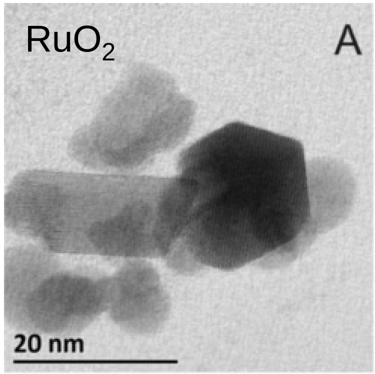
NAP-XPS set-up at BESSY II

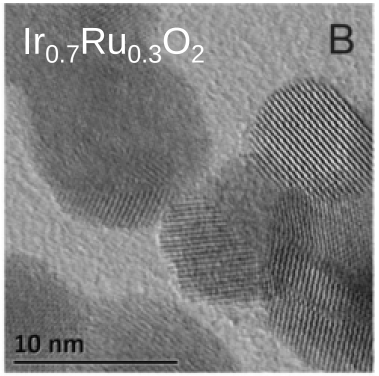
Stabilization mechanism of Ru in $Ir_{0.7}Ru_{0.3}O_2$

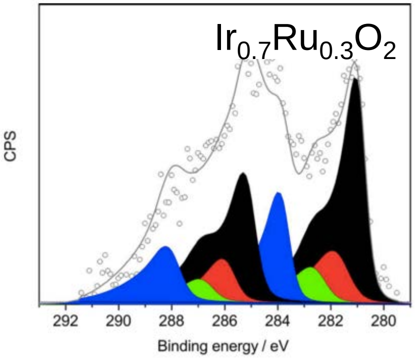
- Near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) allows monitoring of the surface state of MEAs swith RuO_2 and $Ir_{0.7}Ru_{0.3}O_2$ during OER
- Ir protects Ru from the formation unstable hydrous Ru^{IV} oxide
- OER occurs through a surface Ru^{VIII} intermediate

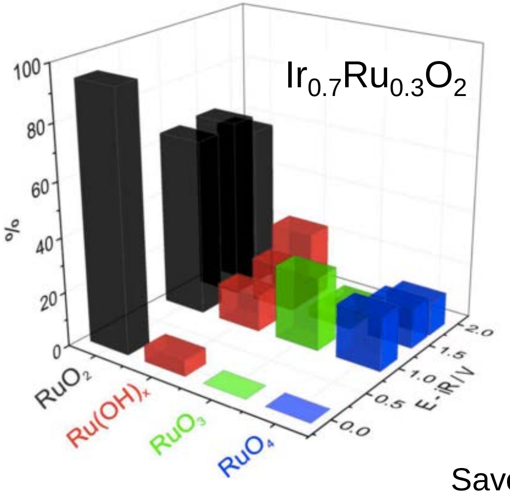


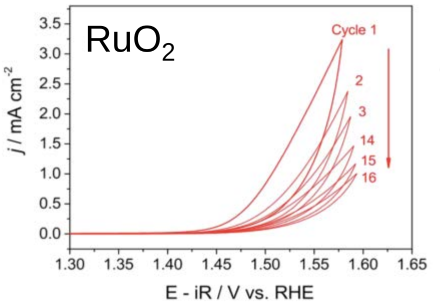


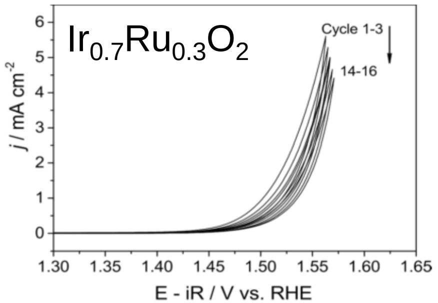












Saveleva *et al.* J. Phys. Chem. Lett., **2016**, *7*, 3240–3245

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

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FCH

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