

# Anode Electrocatalysis for PEM Electrolyzers: Addressing the Challenges of High Activity, Stability and Cost Effectiveness

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## 1. Introduction

Proton exchange membrane (PEM) water electrolysis (EL) is considered as one of the most promising technologies for hydrogen production from renewable energies, which has a potential to penetrate the market in near future and enable the Power-to-Gas (P2G) application on a wider scale (Fig. 1). However, reducing capital cost of PEM electrolyzers without losing efficiency is one of its most pressing challenges. Detailed cost analysis has shown that under future scenarios with high share of renewables, limited operation of 2000-3000 h per annum electricity (OPEX) and investment cost (CAPEX) are of equal importance for P2G plants [1]. A recent study funded by FCH-JU demonstrates that the CAPEX of PEMEL stacks – which however depends on the specific stack design – are dominated by the cost of bipolar plates [2]. In addition also current collectors contribute also significantly to the cost of the stack whereas the catalysts are presently of minor importance. Nevertheless, there is a wide perception that the anode catalysts may be the real hindrance for this technology. One reason is the sluggish oxygen evolution reaction (OER) kinetics on most electrocatalysts and their insufficient durability due to the highly corrosive working environment [3]. To date, Ir-based catalyst is still the only feasible option to promote OER in the anode of a PEM electrolyzer due to its high activity and considerable stability. Still, the most often used catalysts are stable but not very active rutile IrO<sub>2</sub>. Not only the high cost of the precious metal, but also the scarcity of Ir in the earth crust are barriers on the road to commercialization of PEM electrolyzers. Therefore, highly active and stable OER catalysts in acid electrolyte with ultra-low Ir loading are required to address this issue.

In the introduction the current state of the art and the work addressing cost reduction for bipolar plates and current collectors will be shortly addressed. After that the work specifically on electrocatalyst development will be presented.

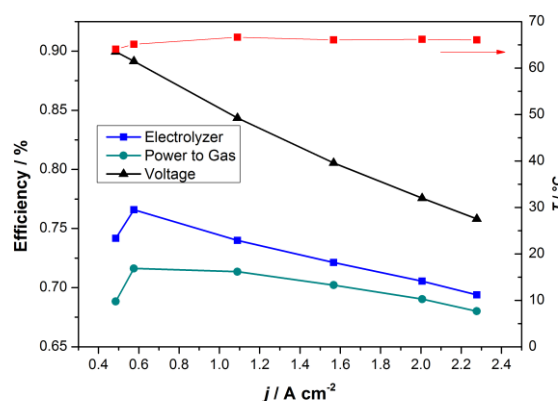


Fig. 1. Efficiency of a 1 MW PEMEL for P2G application at Reitbrook Germany (courtesy of Uniper and partners [4])

## 2. Approach

Generally, there are two approaches to improve an electrocatalyst activity: i) increasing the intrinsic activity of each active site; ii) increasing the number of active sites on a given electrode. Interestingly, a screening study of different technical membrane electrode assemblies in a rainbow stack revealed that Ir-black exhibited a much higher activity compared to common rutile Ir oxides, while it is still sufficiently stable for the PEM electrolysis application. As a consequence Ir-black with IrO<sub>x</sub> surface and metallic core is our benchmark catalysts. Under this frame, amorphous IrO<sub>x</sub> nanoparticles are prepared to achieve a high intrinsic activity, displaying five-fold higher OER activity than commercial Ir-black [5]. The structure and activity of this nanoscale iridium catalyst, in comparison to Ir-black, are shown in In Fig. 2 and Fig.3, respectively,.

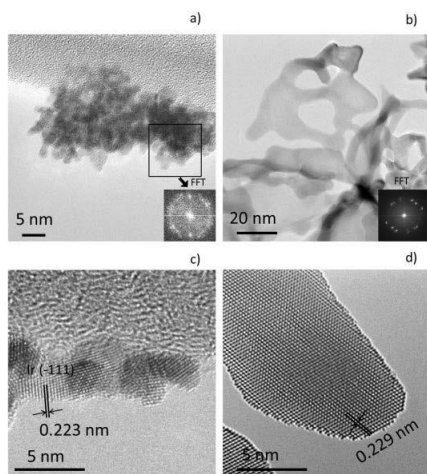


Fig. 2. TEM and HRTEM micrographs of Ir-nano (a), (c) and Ir-black (b), (d).

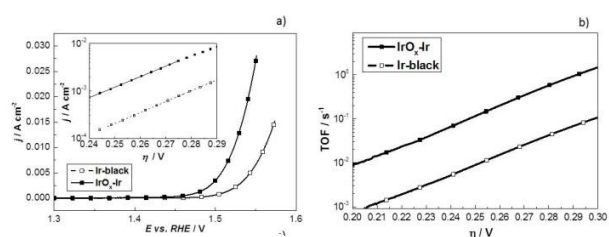


Fig. 3. Current-potential (a), turn-over-frequencies (b) of Ir-nano and Ir-black. Sweep rates of  $5 \text{ mV s}^{-1}$  in Ar-saturated  $0.5 \text{ M H}_2\text{SO}_4$  electrolyte.

In addition, a highly active Ir electrocatalyst derived from amorphous  $\text{IrRuO}_x$  via an electrochemical way was developed, which demonstrates 13 times higher OER activity compared to the rutile phase of  $\text{IrRuO}_2$ . The stability was evaluated by PEM electrolyzer measurements, showing no cell potential decrease during ca. 400 h test. The results are demonstrated in Fig. 4.

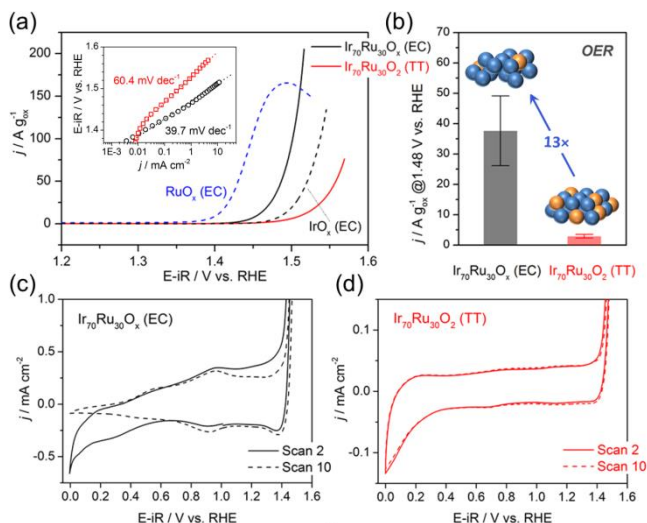


Fig. 4. Current-potential (a), mass activity @  $1.48 \text{ V}$  vs. RHE (b), cyclic voltammetry (c,d) of amorphous  $\text{IrRuO}_x$  and rutile  $\text{IrRuO}_2$ . Sweep rates of  $5 \text{ mV s}^{-1}$  in  $\text{N}_2$ -saturated  $0.05 \text{ M H}_2\text{SO}_4$  electrolyte.

Regarding the second approach, DLR takes electroconductive ceramics as supporting materials to increase the active sites number, thus achieve an improved Ir utilization. First,  $\text{IrO}_x$  was deposited on Magnéli phase  $\text{Ti}_4\text{O}_7$  showing a

better OER activity in terms of Ir mass relative to Ir-black [6]. Further on,  $\text{SnO}_2\text{:Sb}$  aerogel (developed by Armines) was introduced as a support. By taking advantage of the highly porous structure of the aerogel support,  $\text{Ir/SnO}_2\text{:Sb}$ -aerogel allows a decrease of more than 70 wt.% precious metal usage in the catalytic layer, while keeping the same activity and significantly enhancing the stability compared to its unsupported counterpart [7].

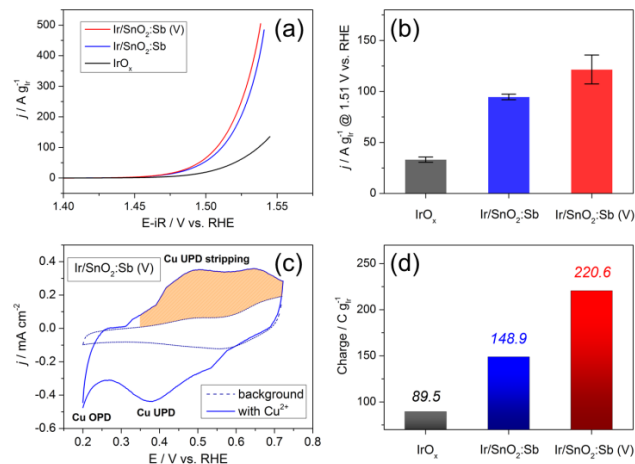


Fig. 5 (a) OER activity performance of  $\text{Ir/SnO}_2\text{:Sb (V)}$ ,  $\text{Ir/SnO}_2\text{:Sb}$  and unsupported  $\text{IrO}_x$ ,  $25^\circ\text{C}$ ,  $\text{N}_2$ -saturated  $0.05 \text{ M H}_2\text{SO}_4$ ,  $5 \text{ mV s}^{-1}$ , 1600 rpm; (b) mass activity comparison under an overpotential of 280 mV; (c) Cu-UPD profile of  $\text{Ir/SnO}_2\text{:Sb (V)}$ ; (d) charge comparison based on Cu-UPD stripping peaks among three catalysts.

In collaboration with the University of Strasbourg advanced in operando techniques, in particular near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS), are applied to provide insight into the potential-dependent specific chemical state of the catalysts surface and explore their electrocatalysis and stabilization mechanisms [8].  $\text{RuO}_2$  and  $\text{IrRuO}_2$  were investigated under water splitting condition in the form of the Aquivion-based membrane electrode assemblies (MEA) and results will be discussed.

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