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Anode catalysts for PEM electrolyzers: Synthesis, Activity and Degradation Aspects with Ex Situ and In Situ Characterization

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Summary. In this presentation, our strategies toward developing high performance oxygen evolution reaction (OER) catalysts will be summarized; as-developed catalysts were investigated from nano scale to system level; in operando near-ambient pressure XPS technique was applied for electrocatalysis mechanism exploration.

Abstract. Proton exchange membrane (PEM) water electrolysis 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 P2G application on a wider scale. However, one of the main hurdle for PEM electrolysis is the anode catalyst because of the sluggish OER kinetics and its insufficient durability due to the highly corrosive working environment.[1] 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. 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.

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. Under this frame, amorphous IrO_x nanoparticles are prepared to achieve a high intrinsic activity, it displays five-fold higher OER activity than commercial Ir-black.[2] In addition, a highly active Ir electrocatalyst derived from amorphous $IrRuO_x$ via an electrochemical way was developed, which demonstrates 13 times higher OER activity compared to the rutile phase of $IrRuO_2$. The stability was evaluated by PEM electrolyzer measurements, showing no cell potential decrease during ca. 400 h test. With the second approach, DLR takes electro-conductive ceramics as supporting materials to increase the active sites number, thus achieve an improved Ir utilization. First, IrO_x was deposited on Magnéli phase Ti_4O_7 showing a better OER activity in terms of Ir mass relative to Ir-black.[3] Further on, SnO_2 :Sb aerogel (developed by Armines) was introduced as a support. By taking advantage of the highly porous structure of the aerogel support, Ir/SnO_2 :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.[4]

The advanced in operando technique, near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS), is applied to provide insight into the potential-dependent specific chemical state of the catalysts surface and explore their electrocatalysis and stabilization mechanisms. RuO_2 and $IrRuO_2$ were investigated under water splitting condition in the form of the Aquivion-based membrane electrode assemblies (MEA), demonstrating that unstable hydrous Ru(IV) oxide formed on the surface already before the OER region mainly contributes to the fast dissolution of RuO_2 , while its formation was hindered by the presence of Ir in the case of $IrRuO_2$.[5] Furthermore, the surface analysis of amorphous IrO_x compared to the rutile phase of IrO_2 under the same conditions will also be discussed.

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