

Electrode Catalyst Development and Electrolyte Engineering for Practical Membrane Electrode Water and CO₂ Electrolysis

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Abstract

Iridium (Ir) and ruthenium (Ru)-based oxygen evolution reaction (OER) catalyst remains to be the go-to anode materials when it comes to commercialized practical proton exchange membrane water electrolysis (PEMWE) regardless of their scarcity and high cost. Since demand is expected to increase substantially in the near future, development of ultra-low precious group metal loaded, Ir in particular, is a very pressing issue for lowering the capital cost for gigawatt scale systems. However, durability problems become severe under low Ir-loaded conditions, posting great limitations in the reduction of Ir-usage. Ru-based catalysts, on the other hand, suffer from poor stability even though they possess the highest onset potential for the acidic OER reactions. In recent years, we have been devoted in addressing these challenges for Ir- and Ru-based acidic OER catalysts. For ultra-low Ir-loaded PEMWE, we demonstrated through the strong catalyst-support interactions, fine IrO_x nanoparticle catalysts formed on the tungsten oxide nanowire (WO_xNW) support delivered compelling OER performance and durability. Furthermore, with the aid of synchrotron-based XPS, suppressed over-oxidation of Ir to >4+ states was observed *in-situ*, giving first-hand information on the actual surface state of working catalyst which is hard to achieve otherwise. This WO_xNW supported IrO_x catalyst was also applied as the anode for single cell testing, delivering and compelling performance under a ultra-low loading of 0.3 mg_{Ir}/cm² and an impressive durability over 200 h at 1A/cm². For the Ru-based catalyst, we investigated the doping effects of various transition and late transition metals to ruthenium-tin (Ru-Sn) mixed rutile oxide. A screening study was applied on Mn, Mo, Ti, Co, W, and Zn-doped Ru-Sn oxides. X-ray absorption spectroscopy (XAS) has been an indispensable and powerful tool to verify the local coordination structure of these doped Ru-Sn oxides and understand them better. Among the screened transition metals, Zn-doped Ru-Sn oxide deliver the highest activity and stability. Extended X-ray absorption fine structure (EXAFS) suggests Zn atoms had the same coordination structure as the Ru and Sn sites. Which provided a clear picture for future modeling studies to explain its impact on the reduced valence of Ru and increased activity and stability at high current densities. When it comes to practical PEMWE, the electrode architecture design becomes increasingly important for ultra-low Ir loaded anodes. From our engineering study, positioning the active components at the right place makes a significant difference in its effective utilization.

Hydrated cations play an important role in the adsorption and activation of CO₂ during its electrochemical reduction. The inhibition of hydrogen evolution in the presence of large alkali cations with small hydration shells is a well-acknowledge phenomenon. Leveraging these pioneering works and ideas, we have explored the use of alkali cations to aid the development of CO₂ reduction catalysts and electrolysis systems. We will first showcase the use of cations to obtain facet-controlled copper nanocrystals catalyst and then shift gears to present a sustainable and durable pure water and CO₂-fed electrolyzer enabled by cation-preengineered cathodes. Alkali cations were discovered to govern the micro local environment of the electrolyte/electrode interface which is vital for CO₂ adsorption and subsequent activation. Such phenomena can also be leveraged to develop neat electrosynthesis methods to obtain shaped nanocrystals of copper with ultra-clean surfaces. Specifically, copper nanocubes enclosed with (100) surfaces that facilitate CO₂-to-C₂₊ transformation can be obtained facilely by electrodeposition. *In-situ* infrared spectroscopy and density functional theory calculations reveals the enhanced selective adsorption of CO₂ in the presence of large alkali cations, yielding well-defined copper nanocubes that favors C₂₊ formation with >80% Faradaic efficiency at 300 mA/cm². Cations not only affect CO₂ adsorption, but also significantly affect the transport of CO₂ in the cathode and showcase our pure water-fed CO₂ electrolyzer. Using cathodes with pre-engineered cations, the bipolar electrolyzer can be operated using pure water and CO₂ as feeds, which eliminates flooding and salt precipitation issue due to crossovered cations to the cathode. With the simple diagnostic methods, we showed how the different cations used to

engineer the cathode can have a dramatic impact in the CO₂ transport properties. With the Cs-engineered cathode, we have achieved the >90% CO Faradaic efficiency at 500 mA/cm² and demonstrated over 165 hr single pass stability at 200 mA/cm² with CO Faradaic efficiency maintained above 80 %

Keywords – Iridium, ruthenium, oxygen evolution reaction, in-situ XPS, PEMWE

References

1. L-Y. Chueh, C-H. Kuo, R-H. Yang, D-H. Tsai, M-H. Tsai, C-C. Yang, H-Y. Chen, C-H. Wang, Y-T. Pan*, WO_x Nanowire Supported Ultra-Fine Ir-IrO_x Nanocatalyst with Compelling OER Activity and Durability, *Chem. Eng. J.*, **2023**, 464, 142613.
2. Y-W. Hsu, H-I. Chang, Y-T. (Frank) Pan*, Active and durable proton exchange membrane water electrolyzer anode with spatially positioned catalytic components, *J. Power Sources*, **2025**, 656, 238107.
3. W-T. Tu, T-H. Tsai, Y-T. Xie, D-H. Tsai, H-Y. Liu, M-K. Tsai*, T-C. Chou*, Y-T. (Frank) Pan*, Cation- and CO₂-assisted electrochemical synthesis of clean, shaped Cu nanocrystals for selective CO₂ reduction to C₂₊ products, *J. Mater. Chem. A*, **2025**, 13, 34827-34835.
4. T-W. Huang, T-H. Tsai, K-H. Kuo, J-A. Hsu, D-H. Tsai, W-T. Tu, C-A. Chen, H-L. Kuo, M-K. Tsai, Y-T. (Frank) Pan*, Sustainable and durable pure water-fed CO₂ electrolysis through cathode cation engineering, *Chem. Eng. J.*, **2026**, 535, 175696.