

Electrochemical methods to assess the water splitting process using electro catalysts

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Abstract:

Fuel cells (FC) are the frontier renewable devices which use hydrogen as a fuel along with other supplies. These energy devices offer the maximum output efficiency but lack commercialization due to transportation and other problems. Solid oxide fuel cells (SOFCs) are considered as the robust energy devices which can overcome these hurdles. SOFCs need a continuous supply of a fuel like H₂, methanol, etc. Water splitting (WSR) is a major source of H₂ and finds a big place in the current publications about advanced materials.

The nanomaterial's which can catalyse the water splitting reaction in a facile manner and give steady and stable reaction output, are considered as electro catalysts. The cyclic voltammetry (CV) and linear sweep voltammetry (LSV) are the modern electro analytical techniques used for water splitting which characterize the nanomaterial for their inherent catalytic properties to cause either oxygen evolution reaction (OER) or hydrogen evolution reaction (HER). The electrochemical parameters based on these methods can validate towards the use of nanomaterial for WSR and corroborated by electrochemical impedance spectroscopy (EIS).

Based on the Nernst equation, acidic conditions are favorable toward HER, while OER proceeds more easily in alkaline media. Therefore, most efforts in developing HER and OER electrocatalysts are conducted in acidic and alkaline electrolytes, respectively. However, in order to accomplish water electrolysis, both HER and OER electro catalysts are preferred to function in the same electrolyte. The disparity of conditions during the development stage of HER and OER catalysts will likely result in complicated integration and mediocre performance for full water splitting.²⁸ With these considerations in mind, our group is interested in developing nonprecious bifunctional electrocatalysts for both HER and OER in the same electrolyte to achieve efficient overall water electrolysis, due to the advantages of simplifying the electrolyser configuration and reducing the overall cost. Owing to the nature of a four-electron process, the over-potential of OER is typically much higher than that of HER to afford same current density, therefore the overall efficiency of water splitting in alkaline media would be better than that in acidic media. Moreover, most earth-abundant OER catalysts cannot survive strong acidic electrolytes. Following our previous success in preparation of CoS_x²⁹ and NiS_x films³⁰ via electrodeposition, a similar potentiodynamic deposition was conducted to obtain Co-P film by consecutive linear scanning between -0.3 and -1.0 V vs. Ag/AgCl at a scan rate of 5 mV s⁻¹ and a rotation speed of 500 rpm under stirring in the stock solution (50 mM CoSO₄, 500 mM NaH₂PO₂, and 100 mM CH₃COONa in water).⁸ Scanning electron microscopy (SEM) image and the cross-section SEM image of Co-P reveal nearly complete coverage of Co-P on a copper substrate and thickness of 1–3 μm. Linear sweep voltammetry (LSV) was conducted to investigate the electro-catalytic

HER, OER, and overall water splitting performance of Co-P in 1.0 M KOH. As depicted in Figure 3b, inset, the HER polarization curve of Co-P demonstrates an onset potential of approximately -50 mV vs. the reversible hydrogen electrode (RHE), slightly more negative than that of Pt/C (~0 mV vs RHE). However, the catalytic current density of Co-P quickly surpasses that of Pt/C beyond -167 mV vs. RHE highlighting its remarkable HER activity. Co-P requires an overpotential of only 94 mV to reach 10 mA cm⁻² and features a small Tafel slope of 42 mV dec⁻¹, representing an impressive performance for HER under alkaline conditions. The SEM image of Co-P after 24 h electrolysis (post-HER Co-P) confirms the retention of its morphology, implying its robust stability for long-term H₂ evolution. Subsequently, its OER performance was assessed in the same electrolyte (1.0 M KOH). Co-P achieves 10 mA cm⁻² at an overpotential of 345 mV (Figure 3d), lower than those of IrO₂ and many other nonprecious OER catalysts. In contrast to the uniform morphology of the fresh and post-HER Co-P, the SEM image of the post-OER Co-P indicates particle aggregates. Further characterizations reveal the oxidation of both Co and P during OER.⁸ Therefore, the real active sites for OER are attributed to the in situ generated cobalt oxides and (oxy)hydroxides on the bulk Co-P film. Finally, a water electrolyser using Co-P as the electrocatalyst (or catalyst precursor) on both anode and cathode was assembled and tested in 1.0 M KOH. The Co-P catalyst couple demonstrates a cell voltage of only 1.744 V to afford 100 mA cm⁻², even lower than that of the Pt/C and IrO₂ couple (Figure 3f). Analogous bifunctional performance for overall water splitting can be obtained from electrodeposited Ni-P film as well.⁹ In order to accelerate electrocatalytic kinetics and lower the required overpotential, an electrocatalyst with optimal reaction interfaces is critical for both triphase HER and OER (solid, liquid, and gas).^{10–12} Within this scenario, catalysts featuring large specific surface area, open porous structure, and high accessibility of active sites are anticipated to be beneficial to electrocatalytic performance.^{10–12} Therefore, we synthesized three-dimensional (3D) hierarchically porous Ni₂P superstructures on Ni foam (Ni₂P/Ni/NF) as nonprecious bifunctional electrocatalysts for overall water splitting.¹⁰ Ni₂P/Ni/NF was prepared through a template-free electrodeposition of porous metallic Ni microsphere arrays on a Ni foam (Ni/NF) followed by phosphorylation (Figure 4a). SEM images corroborate its hierarchical macroporosity and urchin-like morphology. The cell voltage of a Ni₂P/Ni/NF-based electrolyser at 10 mA cm⁻² is 1.49 V, much lower than those of Co-P (1.64 V)⁸ and Ni-P (1.67 V).⁹ The exceptional activity of Ni₂P/Ni/NF is ascribed to its unique superstructure. The 3D hierarchically macro porous structure with interconnected configuration not only provides high accessibility of active sites but also buffers electrolyte to facilitate ion transport and gas diffusion.^{31,32} In addition, we also explored nickel sulfides as functional electro catalysts for overall water splitting. High-

temperature sulfurization of Ni/NF can readily achieve 3D hierarchically porous NiS_x super structures. The hp-NiS_x possesses both macro pores and mesopores, in contrast to Ni₂P/Ni/NF with singular macro pores. The hp-NiS_x electrocatalyst couple only requires a voltage of 1.47 V to reach 10 mA cm⁻² for overall water electrolysis. Benefiting from high specific surface area, controllable pore texture, and modular organic and inorganic components, metal-organic frameworks (MOFs) represent promising candidates to obtain competent electrocatalysts.^{12,33,34} We first reported a MOF-derived route to produce mesoporous Co-P/NC Nano polyhedrons composed of CoP_x Nano particles embedded in N-doped carbon matrices as bifunctional electrocatalysts for both HER and OER.¹² The Co-P/NC was prepared by direct carbonization of Co-based zeolitic imidazolate frameworks (ZIF-67) followed by

phosphorylation (Figure 4d). SEM images of Co-P/NC suggest its inheritance of the polyhedron-like morphology of ZIF-67 (Figure 4e). Elemental mapping results confirm the presence of Co, P, N, and C in Co-P/NC, and P is highly localized with Co, consistent with the formation of CoP_x. The specific surface area of Co-P/NC is 183 m²g⁻¹, larger than that of hp-NiS_x (11 m²g⁻¹).¹¹ As expected, Co-P/NC exhibits remarkable HER and OER activities and affords a current density of 165 mA cm⁻² at 2.0 V for overall water splitting. ^{4f} compares the cell voltages of overall water electrolysis based on our reported functional electrocatalysts at different current densities, including the Pt/C and RuO₂ couple as a reference. Such a functional electrocatalyst strategy for overall water splitting can be readily extended to other transition metal and noble metal derivatives and even metal-free Nano carbons.