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 evaluation reaction (OER) or hydrogen evaluation 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 favorabletoward HER, while OER proceeds more easily in alkaline media. Therefore, most efforts in developing HER and OERelectrocatalysts 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.28With these considerations in mind, our group is interested in developing nonpreciousbifunctional electrocatalysts for both HER and OER in thesame 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 toafford same current density, therefore the overall efficiency of water splitting in alkaline media would be better than that inacidic media. Moreover, most earth-abundant OER catalystscannot survive strong acidic electrolytes.Following our previous success in preparation of position, CoSx29andNiSxfilms30via electrode а similar potentiodynamicdeposition was conducted to obtain Co-Pfilm by consecutive linear scanning between -0.3 and -1.0 V vs. Ag/AgCl at a scan rate of 5 mV s-1and a rotation speed of 500 rpm under stirringin the stock solution (50 mM CoSO4, 500 mM NaH2PO2, and100 mM CH3COONa in water).8Scanning electron micros-copy (SEM) image and the cross-section SEM image of Co-Preveal nearly complete coverage of Co-P on a copper substrate and thickness of 1-3µm. Linear sweep voltammetry (LSV) was conducted to investigate the electro-catalytic

HER, OER, and overall water splitting performance ofCo-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 (~0mVvsRHE). However, the catalytic current density of Co-P quicklysurpasses that of Pt/C beyond -167 mV vs. RHE highlighting its remarkable HER activity. Co-P requires anoverpotential of only 94 mV to reach 10 mA cm-2and features small Tafel slope of 42 mV dec-1, representing an impressive performance for HER under alkaline conditions. The SEMimage of Co-P after 24 h electrolysis (post-HER Co-P)confirms the retention of its morphology, implying its robust stability for long-term H2evolution. Subsequently, itsOER performance was assessed in the same electrolyte (1.0 MKOH). Co-P achieves 10 mA cm-2at an overpotential of 345mV (Figure 3d), lower than those of IrO2and many othernonprecious OER catalysts. In contrast to the uniformmorphology of the fresh and post-HER Co-P, the SEMimage of Co-P the post-OER indicates particle aggregates. Further characterizations reveal the oxidation of both Co and P during OER.8Therefore, the real active sites forOER are attributed to the in situ generated cobalt oxides and(oxy)hydroxides on the bulk Co-Pfilm. Finally, a water electrolyser using Co-P as the electrocatalyst (or catalystprecursor) on both anode and cathode was assembled and tested in 1.0 M KOH. The Co-P catalyst couple demonstrates acell voltage of only 1.744 V to afford 100 mA cm-2, evenlower than that of the Pt/C and IrO2couple (Figure 3f). Analogous bifunctional performance for overall water splittingcan be obtained from electrodeposited Ni-Pfilm as well.9In order to accelerate electrocatalytic kinetics and lower therequired overpotential, an electrocatalyst with optimal reactioninterfaces is critical for both triphase HER and OER (solid,liquid, and gas).10-12Within this scenario, catalysts featuringlarge specific surface area, open porous structure, and highaccessibility of active sites are anticipated to be beneficial toelectrocatalytic performance.10-12Therefore, we synthesizedthree-dimensional (3D) hierarchically porous Ni2P superstructures on Ni foam (Ni2P/Ni/NF) as nonprecious bi functional electrocatalysts for overall water splitting.10Ni2P/Ni/NFwas prepared through a template-free electrodeposition of porous metallic Ni microsphere arrays on a Ni foam (Ni/NF)followed by phosphorylation (Figure 4a). SEM imagescorroborate its hierarchical macroporosity and urchin-like morphology. The cell voltage of a Ni2P/Ni/NF-based electrolyser at 10 mA cm-2is 1.49 V, muchlower than those of Co-P (1.64 V)8and Ni-P (1.67 V).9Theexceptional 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.31,32In addition, we also explored nickel sulfides as functional electro catalysts for overall water splitting. High-

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temperature sulfurization of Ni/NF can readily achieve 3D hierarchically porous NiSx super structures. The hp-NiSxpossessesboth macro pores and mesopores, in contrast to Ni2P/Ni/NFwith singular macro pores. The hp-NiSxelectrocatalyst couple only requires a voltage of 1.47 V to reach 10 mA cm-2 foroverall water electrolysis. Benefiting from high specific surface area, controllable poretexture, and modular organic and inorganic components. metal-organic frameworks (MOFs) represent promisingcandidates to obtain competent electrocatalysts.12.33,34Wefirst reported a MOF-derived route to produce mesoporousCo-P/NC Nano polyhedrons composed of CoPx Nano particlesembedded in N-doped carbon matrices as bifunctionalelectrocatalysts for both HER and OER.12The Co-P/NC was prepared by direct carbonization of Co-based zeoliticimidazolate frameworks (ZIF-67) followed bv

phosphorylation(Figure 4d). SEM images of Co–P/NC suggest its inheritanceof the polyhedron-like morphology of ZIF-67 (Figure 4e).Elemental mapping results confirm the presence ofCo, P, N, and C in Co–P/NC, and P is highly localized withCo, consistent with the formation of CoPx. The specific surface area of Co–P/NC is 183 m2g–1, larger than that of hp-NiSx(11 m2g–1).11As expected, Co–P/NC exhibits remarkable HER and OER activities and affords a current density of 165mA cm–2at 2.0 V for overall water splitting. 4fcompares the cell voltages of overall water electrolysis based on our reported functionalelectro catalysts at different current densities, including the Pt/C and RuO2couple as a reference. Such a functionalelectro catalyst strategy for overall water splitting can be readily extended to other transition metal and noble metal derivatives and even metal-free Nano carbons.