Development of high-performance and stable electrocatalysts for alkaline water electrolysis

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OBJECTIVES AND NOVELTY

Water electrolysis, powered by renewable energy, has been regarded as the most promising approach for high-purity H_2 production. However, slow kinetics in the Hydrogen Evolution Reaction (HER) and Oxygen Evolution Reaction (OER) result in significant overpotential, hindering mass hydrogen production. Thus, efficient electrocatalysts are required to expedite the process. To date, the most effective electrocatalysts are primarily based on noble metals such as Pt, Ir- and Ru and their derivatives. However, their scarcity and high cost hinder their sustainable use in large-scale applications. Hence, it is crucial to pursue cost-effective and high-performance electrocatalysts for practical alkaline exchange membrane water electrolysis.

This Doctoral Thesis primarily focuses on investigating and designing bimetallic electrocatalysts for OER and HER electrodes utilizing earth-abundant transition metals. Ni, Fe, and Co were selected as precursor materials due to their favorable performance and cost-effectiveness. Combining these active metals with conductive carbon materials can lead to intriguing properties by adjusting electronic structure, morphology, and particle size – crucial factors for catalysis. Bimetallic combinations can exhibit higher activity than single metals, thanks to synergistic effects. Additionally, depositing metals on a 3D conductive substrate enhances their activity by forming a thin, highly conductive layer, thereby improving mass transfer during the reaction.

RESULTS

Two spinel structures, $NiFe_2O_4$ and $CoFe_2O_4$, were modified through integration with carbon. The metal oxides were prepared using a hydrothermal route, and the as-prepared bimetallic oxides underwent further modification through in-situ polymerization, followed by carbonization. Polydopamine (PD) was selected as the ideal carbon source and surface functionalizing agent. PD contains diverse functional groups (e.g., catechol, imine, amine) and offers eco-friendly, cost-effective material modification. PD transforms into nitrogen-doped graphitized carbon at high pyrolysis temperatures, enhancing electrical conductivity through improved graphitization and electron transport. Nitrogen-doped carbon-coated CoFe and NiFe electrocatalysts were synthesized via hydrothermal method and dopamine-based in-situ polymerization, followed by carbonization. The

as-prepared $CoFe_2O_4$ powder was combined with various dopamine content (10, 20, 30, and 40 wt. %). Controlled optimization led to the $CoFe_2O_4$ spinel structure changing to carbon-coated CoFe alloy. The as-prepared electrocatalysts were measured for their electrochemical performance in a three-electrode system controlled by a potentiostat/galvanostat. $CoFe/NC_{30\%}$ electrocatalyst exhibits excellent catalytic activity towards OER in 1M KOH aqueous solution, in which a small overpotential of 340 mV was required to generate 10 mA cm^{-2} accompanied with 24 h durability. Optimal dopamine content attributed to high OER activity and stability due to synergistic CoFe and N-doped carbon coating and reduced charge transfer resistance.

Besides, spinel oxide composed of $NiFe_2O_4$ was prepared and transformed into nitrogen-doped carbon-decorated $Ni_3Fe@NiFe_2O_4$ nanocomposite (denoted as $NiFe/NC_x$) electrocatalysts using the same method. The NiFe electrocatalyst containing 10 wt.% dopamine ($NiFe/NC_{10\%}$) exhibited relatively higher catalytic activity for OER measured in 1M KOH. It revealed a low overpotential (350 mV at 10 mAcm^{-2}), a low Tafel slope (56 mVdec^{-1}), a low charge transfer resistance, and a relatively higher electrochemically active surface area. The most notable feature is that it remained stable for at least 12 hours.

Besides, we developed a promising electrocatalyst by incorporating CoFe into a phosphorus and nitrogen co-doped carbon foam derived from petroleum pitch waste. First, a support material consisting of (P, N) co-doped carbon foam was prepared through a thermo-chemical process; next, the incorporation of mono and bimetals consisting of Co and Fe into the (P, N) co-doped carbon foam was performed, and finally, the resulting composite was subjected to carbonization process. The resulting CoFe@PN-CF electrocatalyst exhibited remarkable performance, including low overpotential (320 mV) at 10 mAcm^{-2} current density, a small Tafel slope (48 mVdec^{-1}), and stability over 20 hours of continuous operation in a 1M KOH solution.

Figure 1a illustrates the OER polarization curve of the top-performing electrocatalyst selected from the aforementioned synthesized materials. The electrocatalysts (CoFe@PN-CF, $CoFe@NC_{30\%}$, and $NiFe/NC_{10\%}$) show enhanced electrocatalytic activity compared to commercial IrO_2. The overpotential needed for a 10 mAcm^{-2} current density evaluation, a benchmark for water electrolysis, is as follows:

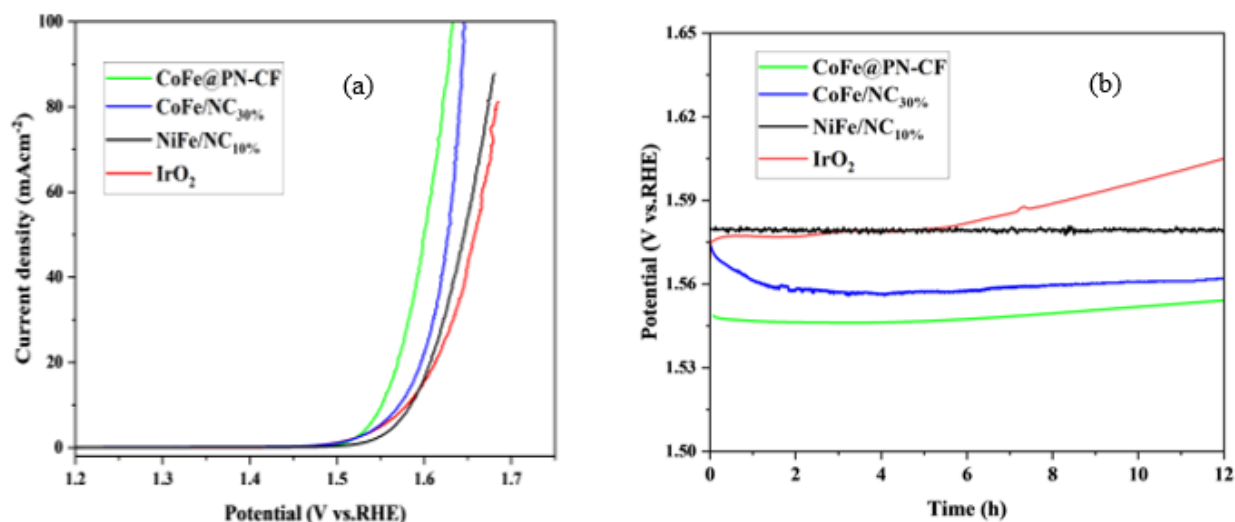**Figure 1.** (a) OER polarization curves, (b) stability test at j = 10 mAcm-2 in 1 M KOH.

CoFe@PN-CF (320 mV), CoFe@NC$_{30\%}$ (340 mV), NiFe/NC$_{10\%}$ (350 mV), and IrO$_2$ (350 mV). Among them, CoFe@PN-CF stands out as the most promising OER electrocatalyst. **Figure 1b** shows the stability result of the best-performing sample. It appears that the as-prepared electrocatalyst displayed relatively high stability for OER, further demonstrating the significant potential for long-term, extensive application.

Apart from the OER electrodes, catalysts for HER were also prepared. Ni and Co metals were grown on the SSM through the hydrothermal and phosphorization process, resulting in NiCoP@SSM catalyst. It showed exceptional hydrogen evolution activity in 1M KOH solution, achieving 10 mA cm-2 current density at a low 138 mV overpotential. The catalyst maintained stability over 24 hours and owed its performance to the porous SSM structure and synergy between metals and phosphorus. This method offers a simple, binder-free way to produce cost-effective HER electrocatalysts using SSM.

To sum up, this Thesis successfully developed three electrocatalysts based on transition metals (CoFe/NC30%, NiFe/NC10%, and CoFe@PN-CF) for OER, along with one electrocatalyst (NiCoP@SSM) for HER, all of which exhibited impressive performance. These electrocatalysts were further assessed in complete single-cell water electrolysis, showcasing noteworthy efficiency, with CoFe@PN-CF displaying relatively enhanced activity.

RELATED PUBLICATIONS

[1] G.A. Gebreslase, M.V. Martínez-Huerta, D. Sebastián, M.J. Lázaro, NiCoP/CoP sponge-like structure grown on stainless steel mesh as a high-performance electrocatalyst for hydrogen evolution reaction, Electrochim. Acta. 438 (2023) 141538.

[2] G.A. Gebreslase, M.V. Martínez-Huerta, D. Sebastián, M.J. Lázaro, Transformation of CoFe2O4 spinel structure into active and robust CoFe alloy/N-doped carbon electrocatalyst for oxygen evolution reaction, J. Colloid Interface Sci. 625 (2022) 70–82.

[3] G.A. Gebreslase, D. Sebastián, M.V. Martínez-Huerta, M.J. Lázaro, Nitrogen-doped carbon decorated-Ni3Fe@Fe3O4 electrocatalyst with enhanced oxygen evolution reaction performance, J. Electroanal. Chem. 925 (2022) 116887.

[4] G.A. Gebreslase, D. Sebastián, M.V. Martínez-Huerta, T. Tsoncheva, B. Tsyntsarski, G. Georgiev, M.J. Lázaro, CoFe-loaded P, N co-doped carbon foam derived from petroleum pitch waste: an efficient electrocatalyst for oxygen evolution reaction; Catalysis Today : doi: 10.1016/j.cattod.2022.12.022

[5] G.A. Gebreslase, M.V. Martínez-Huerta, M.J. Lázaro, Recent progress on bimetallic NiCo and CoFe based electrocatalysts for alkaline oxygen evolution reaction: A review, J. Energy Chem. 67 (2022) 101–137.