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Advanced bifunctional electrocatalyst generated through cobalt phthalocyanine tetrasulfonate intercalated Ni_2Fe-layered double hydroxides for a laminar flow unitized regenerative micro-cell

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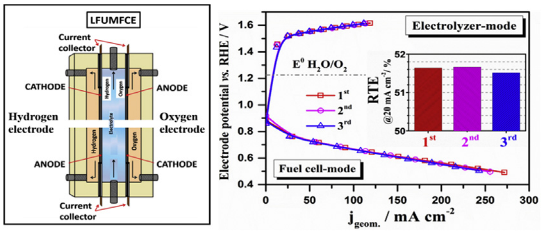
HIGHLIGHTS

- $NiFeO_x/CoN_x$-C electrocatalyst was derived from CoPcTs-intercalated Ni_2Fe- LDH.
- It exhibits excellent ORR/OER bifunctional electrocatalytic activity and stability.
- It shows high performance in a H_2-O_2 laminar flow unitized regenerative micro-cell.
- The strong synergistic effect exists between Co-N_x and $NiFeO_x$ centers.

GRAPHICAL ABSTRACT



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ABSTRACT

We fabricated a $NiFeO_x/CoN_y$-C nanocomposite derived from CoPcTs-intercalated Ni_2Fe-layered double hydroxides (Ni_2Fe-CoPcTs-LDH), which served as high-efficiency, low-cost, and long-durability bifunctional oxygen electrocatalyst in half-cell, and a H_2-O_2 laminar flow unitized regenerative micro-cell (LFURMC) in alkaline media. Based on the synergistic effect between Co-N_y and $NiFeO_x$ centers, the non-noble hybrid catalyst $NiFeO_x/CoN_y$-C achieves a $\Delta E_{(\eta@jOER,10\ -\ \eta@jORR,-3)} = 0.84$ V in alkaline solution, outperforming the commercial Pt/C, and very close to that of IrO_x/C. In the fuel cell mode, the performance of $NiFeO_x/CoN_y$-C with the maximum power density of 56 mW cm^{-2} is similar to that of Pt/C (63 mW cm^{-2}) and IrO_x/C (58 mW cm^{-2}); in the electrolysis mode, the calculated maximum electrical power consumed on $NiFeO_x/CoN_y$-C (237 mW cm^{-2}) is more than 3 times that on Pt/C (73 mW cm^{-2}), similar with that of IrO_x/C. More importantly, the $NiFeO_x/CoN_y$-C shows a remarkable stability in alternating modes in a LFURMC system.

1. Introduction

Increasing inevitable global demands of energy have attracted considerable attention on alternative energy harvesting technologies, conversion and storage systems with high efficiency, cost-effective and environmentally friendly [1], such as, rechargeable metal-air batteries, unitized regenerative cells (URCs), and water splitting electrolyzers [2,3]. The oxygen reduction reaction (ORR) is the ubiquitous cathode reaction in fuel cells, while the oxygen evolution reaction (OER) is the anodic reaction in electrolyzers [4–6]. Thus, in these systems, the conversion between O_2 and H_2O

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is a rate determining step on oxygen electrodes. However, the intrinsic sluggish reaction kinetics, and large overpotential (η) related to ORR and OER greatly hinder their development and commercialization. Up to now, the state-of-art catalyst for ORR consists of Pt-based materials [7–9], while Ru- and Ir-oxides are the best ones for OER. Theses catalysts show only moderate activity towards ORR or OER, that is why, Pt/Ir-IrO_2 [10], and PtIrRu [11] were investigated as bifunctional electrocatalysts. The scarcity of the precious metals, their prohibitive cost, and declining activity greatly hamper the practice for large-scale applications. Therefore, an efficient and stable bifunctional catalyst based on earth-abundant non-noble metals, is practically important for URCs, a promising energy storage system.

Layered double hydroxides (LDHs) compounds, one kind of two-dimensional (2D) anionic clay materials with a general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A_{x/n}]^{n-}mH_2O$ ($X = M^{2+}/(M^{2+}+M^{3+})$, $x = 0.2–0.33$), has been largely investigated as alternative candidates or precursors for applications in energy storage and conversion [12,13], and catalysis [14,15], and as functional additives for polymers [16] due to adjustable chemical composition, exchangeable anions, and tunable charge density. In the LDHs, the high dispersion of M^{2+} and M^{3+} cations in the host sheets, and preferred orientation of exchangeable anions (A^{n-}) in the interlayer region open new opportunities for LDHs as bifunctional oxygen electrode materials. Recently, various reports on mixed-metal oxide (MMO) nanocomposites by thermal treatment of LDH precursors have demonstrated promising OER performance in alkaline medium [12,17,18]. Also, cobalt phthalocyanine (CoPc) with a nitrogen-linked tetrameric diiminoisoindoline conjugated macrocycle is a well-known electrocatalysts for ORR [19,20]. Therefore, a novel strategy for exploring bifunctional electrocatalysts is developed by thermal treatment of intercalated structure LDH containing multiple different catalytic active species.

Herein, we report a new bifunctional electrocatalyst $NiFeO_x/CoN_y$-C composite by simple calcination of Ni_2Fe-CoPcTs-LDH precursor based on the intercalation of cobalt phthalocyanine tetrasulfonate (CoPcTs) into nickel-iron (Ni_2Fe-LDHs), and investigated for the ORR and OER processes in KOH medium. The key aspects of this bifunctional electrocatalyst, for the reversible oxygen electrode, is the mutual incorporation of the ORR-active centres (CoN_y) [21], and OER-active ones (spinel $NiFe_2O_4$) [22], Fig. 1, respectively derived from the interlayer $CoPcTs^{2-}$ anions and the nickel-iron host sheet in the same layered double hydroxide. Here, the intercalation of CoPcTs anions into the interlayer region of Ni_2Fe-LDH favours to enhance the immobilization of CoPcTs. Particularly, the host sheet Ni_2Fe-LDH and the interlayer CoPcTs anions are alternating, which aids to improve dispersion degree of two catalytic sites (CoN_y and $NiFe_2O_4$) and then to increase the catalytic performance [15].

2. Experimental

2.1. Materials

All the chemicals (A.R. grade) were directly used as received. Carbon black was activated under nitrogen atmosphere at 400 °C for 4 h.

2.2. Preparation of $NiFeO_x/CoN_y$-C bifunctional electrocatalyst

The $NiFeO_x/CoN_y$-C bifunctional electrocatalyst was prepared by calcination of Ni_2Fe-CoPcTs-LDH precursor under nitrogen atmosphere at 600 °C for 3 h. The Ni_2Fe-SDS-LDH composite was synthesized by using a method developed in the laboratory [23,24]. For example, a solution A (2:3, $V_{ethanol}/V_{deionized\ water}$) containing 100 mL of 12.5 mmol $Fe(NO_3)_3$, 25 mmol $Ni(NO_3)_2$ and 6.25 mmol sodium dodecyl sulfate (SDS), and a solution B consisting of 50 mL of 75 mmol NaOH were simultaneously added into a colloid mill at 5000 rpm for 5 min. Then the resulting suspension was moved into a Teflon-lined stainless autoclave, which was kept at 140 °C for 24 h. Ni_2Fe-SDS-LDH sample was obtained after 5 centrifugation/washing cycles using deionized water and drying at 60 °C. Secondly, the Ni_2Fe-CoPcTs-LDH precursor was obtained by dispersing 0.1 g Ni_2Fe-SDS-LDH powder in 300 mL of CoPcTs solution (CoPcTs/Fe = 20, mol/mol) at 80 °C under vigorous stirring for 24 h, washed using deionized water, and dried at 60 °C. Finally, the Ni_2Fe-CoPcTs-LDH precursor (the loading amount of CoPcTs for the Ni_2Fe-CoPcTs-LDH is 141 $\mu g/cm^{-2}$) was calcined at 600 °C under inert atmosphere with a ramp rate of 10 °C min^{-1} to obtain $NiFeO_x/CoN_y$-C electrocatalyst.

2.3. Physical-characterization

A Shimadzu XRD-6000 X-ray diffractometer was used to record powder X-ray diffraction (pXRD) patterns using Cu-K_α ($\lambda = 0.154$ nm) at a scanning rate of 10°/2θ min^{-1} at 40 kV and 30 mA. A Vector 22 (Bruker) spectrophotometer was employed to collect the Fourier transform infrared (FT-IR) spectra by the KBr pellet technique from 4000 cm^{-1}–400 cm^{-1} with a resolution of 2 cm^{-1}. A Zeiss Supra 55 scanning electron microscope (SEM) was applied to monitor the morphology and structure of the samples. A VG ESCALAB 2201 XL spectrometer was used to measure X-ray photoelectron spectroscopy (XPS). Nanofinder 3.0 Raman spectrometer (Tokyo Instrument) was employed to examine Raman spectra of these samples with a visible laser beam of 532 nm.

2.4. Electrochemistry

2.4.1. Electrochemical measurements in half-cell

All the electrochemical tests were carried out in a standard

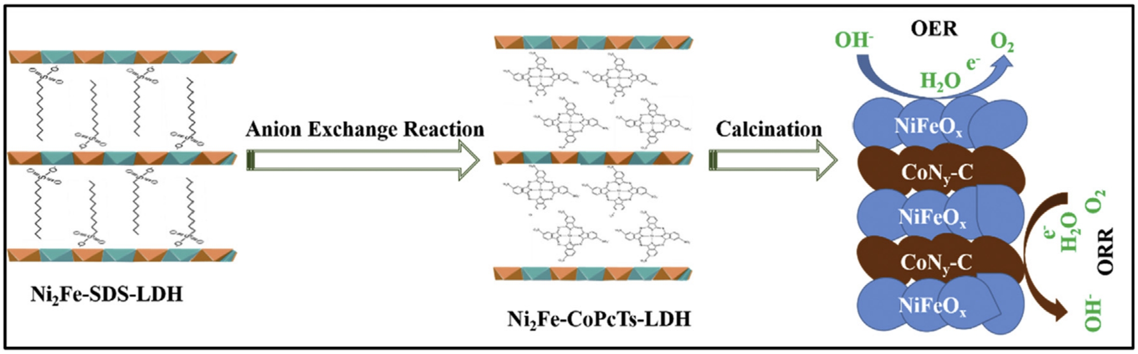

Fig. 1. The chemical route to generate $NiFeO_x/CoN_y$-C electrocatalyst.