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Engineering hybrid between nickel oxide and nickel cobaltate to achieve exceptionally high activity for oxygen reduction reaction

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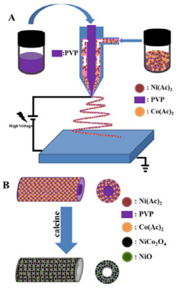
HIGHLIGHTS

- Porous NiO/$NiCo_2O_4$ nanotubes were prepared by coaxial electrospinning-assisted method.
- They exhibit significantly enhanced electrocatalytic activity for ORR.
- The good ORR performance may be attributed to their unique microstructures.

GRAPHICAL ABSTRACT



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ABSTRACT

The porous NiO/$NiCo_2O_4$ nanotubes are prepared via a coaxial electrospinning technique followed by an annealing treatment. The resultant NiO/$NiCo_2O_4$ hybrid is developed as a highly efficient electrocatalyst, which exhibits significantly enhanced electrocatalytic activity, long-term operation stability, and tolerance to crossover effect compared to NiO nanofibers, $NiCo_2O_4$ nanofibers and commercial Pt(20%)/C for oxygen reduction reactions (ORR) in alkaline environment. The excellent electrocatalytic performance may be attributed to the unique microstructures of the porous NiO/$NiCo_2O_4$ nanotubes, such as heterogeneous hybrid structure, open porous tubular structure, and the well dispersity of the two components. Moreover, the promising and straightforward coaxial electrospinning proves itself to be an efficient pathway for the preparation of nanomaterials with tubular architectures and it can be used for large-scale production of catalysts in fuel cells.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been considered as a highly promising power source in future energy systems. However, the common obstacles limiting their broad applications are the high cost and the vulnerability toward reaction poisons of the Pt-based catalysts as well as inherently sluggish kinetics of the oxygen reduction (ORR) on the cathode [1–4]. It is therefore of great significance to develop alternative inexpensive catalysts with high activity and wide availability, such as Pt-based alloys [5,6] and common metals or metal oxides [7,8]. Recently, experimental and theoretical studies showed that mixed metal oxides especially cobalt- and manganese-based oxides are an important class of promising electrocatalysts towards the ORR in alkaline solutions [9]. In contrast to their single

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component, these oxides as electrocatalysts feature a number of advantages, such as high activity, easy availability, low cost, thermodynamic stability, and low electrical resistance. Recently, Chen et al. synthesized spinel-structured $Co_xMn_{3-x}O_4$ nano-crystals, which exhibit considerably high catalytic activity towards ORR as a result of their high surface area and abundant defects. More specifically, the $Co_xMn_{3-x}O_4$ nano-crystals have a specific current density of -43.2 mA mg^{-1} and a transferred electron number of 3.7, both of which are comparable to those of the Pt/C catalyst (-43.9 mA mg^{-1}, 3.9) [10]. Furthermore, hybridizing two different components is an available route for achieving significantly enhanced electrochemical performance. Yang and coworkers reported that Co_3O_4/Co_2MnO_4 nanocomposites exhibit high activity for ORR as a synergistic catalyst, which can be attributed to their large surface area and well-dispersed two-phase heterogeneous structure [11]. In fact, the hybrid materials with a heterojunction, i.e. an interface that occurs between two different types of semiconductors, have been shown to give rise to superior performance in catalysis, electrochemistry, and magnetism when compared to each component. For example, Co_3O_4 nanowire/MnO_2 core/shell nanobelt arrays exhibited significantly enhanced capacity and rate capability, which can be ascribed to the synergistic effect between Co_3O_4 and MnO_2 [12]. However, the synthesis procedure for achieving the hybridization of two components mentioned above, still suffers from disadvantages such as complicated production process and no universal applicability. Therefore, developing a simple, yet high yield strategy to fabricate hybrid materials with a control composition is highly desirable but still very challenging. On the other hand, recent research on nanostructured materials has demonstrated that their oxygen reduction performance could be significantly improved by manipulating the microstructures of the materials [13,14]. For example, porous structure of catalysts may decrease the mass transport resistance and allow the access of the reactant species to the active surface sites easier, which is greatly beneficial for the ORR process. This fact has got solid support from the work reported by Srinivasan et al., in which porous $NiCo_2O_4$ nanotubes (NCO-NTs), nanofibers (NCO-NFs) and nanobelts (NCO-NBs) were prepared. The BET surface area and total pore volume of the NCO-NTs sample are around 36.9 m^2 g^{-1} and 0.22 cm^2 g^{-1}, respectively, which are much larger than those of NCO-NFs (about 16.1 m^2 g^{-1} and 0.06 cm^2 g^{-1}) and NCO-NBs (about 12.7 m^2 g^{-1} and 0.05 cm^2 g^{-1}). As a consequent, the energy density of NCO-NTs is about 1.6 and 2.0 times those of NCO-NFs and NCO-NBs, respectively [13].

Herein, we demonstrate the preparation of porous $NiO/NiCo_2O_4$ nanotubes via a coaxial electrospinning technique followed an annealing treatment. The resultant $NiO/NiCo_2O_4$ hybrid displays a unique porous tubular structure, and that features homogeneous interface/chemical distributions of the two single components (NiO and $NiCo_2O_4$) at the nanoscale. The porous $NiO/NiCo_2O_4$ nanotubes exhibit enhanced activities as an electrocatalyst towards ORR in alkaline solution compared to NiO nanofibers, $NiCo_2O_4$ nanofibers and commercial Pt (20%)/C (20 wt.% platinum on carbon, Johnson Matthey). Although the onset potential for the $NiO/NiCo_2O_4$ sample is close to that of the Pt(20%)/C catalyst, its current density is higher than that of the Pt(20%)/C catalyst and that its durability is also superior to that of the Pt(20%)/C catalyst.

2. Experimental

2.1. Materials and methods

All chemicals used were analytical grade without further purification. Poly(vinylpyrrolidone) (PVP, K90, Mw = 1,300,000) was purchased from Aldrich and cobaltous acetate [$Co(Ac)_2 \cdot 6H_2O$], nickelous acetate [$Ni(Ac)_2 \cdot 6H_2O$], and *N*,*N*-dimethylformamide (DMF) were acquired from Sinopharm Chemical Reagent Co., Ltd.

2.1.1. Preparation of porous $NiO/NiCo_2O_4$ nanotubes

The porous $NiO/NiCo_2O_4$ nanotubes were fabricated by coaxial electrospinning followed by annealing treatment. In a typical procedure, a solution containing $Co(Ac)_2 \cdot 6H_2O$, $Ni(Ac)_2 \cdot 6H_2O$ and PVP was used as the precursor for the outer channel of the nozzle during the coaxial electrospinning process. This solution was prepared by dissolving $Co(Ac)_2 \cdot 6H_2O$ (0.4 g), $Ni(Ac)_2 \cdot 6H_2O$ (0.4 g) and PVP powder (1.5 g) in DMF (10 g) by vigorous stirring at room temperature for at least 6 h. In a similar way, the inner solution was prepared by dissolving 15 wt.% of PVP in DMF followed by vigorous stirring for 6 h. The inner solution was loaded into the syringe connected to the inner channel of a dual nozzle, which consists of two stainless-steel tubes with the diameters of 1.3 mm (outer) and 0.3 mm (inner). The outer solution in the other syringe was connected to the outer channel of the same dual-nozzle through a Teflon tube. The feeding rates of outer and inner solution are 0.6 and 0.1 mL h^{-1}, respectively. At room temperature a high voltage of 12–15 kV was applied to the dual-nozzle, and the distance between coaxial spinneret tip and collector (aluminum foil) was 15 cm. The as-electrospun nanofibers were peeled off from the collector and then they were transferred into an alumina tube furnace for stabilization. The stabilized sample was annealed at 600 °C in air atmosphere for 3 h at a heating rate of 1 °C min^{-1} to yield final porous $NiO/NiCo_2O_4$ nanotubes.

2.1.2. Preparation of $NiCo_2O_4$ nanofibers and NiO nanofibers

The $NiCo_2O_4$ nanofibers were preparation in a similar way. Briefly, a solution containing stoichiometric $Co(Ac)_2 \cdot 6H_2O$ (0.70 g), $Ni(Ac)_2 \cdot 6H_2O$ (0.35 g) and PVP (1.5 g) in DMF (10 g) was used as outer precursor solution, and 15 wt.% of PVP in DMF was used as inner precursor solution. The feeding rates of outer and inner solutions are 0.6 and 0.1 mL h^{-1} with a high voltage of 12–15 kV and 15 cm distance. The annealing process is similar to that for the porous $NiO/NiCo_2O_4$ nanotubes, but the calcination temperature is 450 °C. NiO nanofibers were fabricated by the same way to the above, just using only one metal salt [$Ni(Ac)_2 \cdot 6H_2O$].

2.2. Characterizations

The composition and phase purity of the as-synthesized samples were analyzed by powder X-ray diffraction (XRD) with Cu Kα ($\lambda = 1.54178$ Å) incident radiation by a Shimadzu XRD-6000 operated at 40 kV voltage and 50 mA current. The size and morphology of the resulting products were studied by a H-8100 transmission electron microscopy (TEM) operating at 200 kV accelerating voltage. The field emission scanning electron microscopy (FE-SEM) of the sample was taken on Hitachi S-4800 SEM unit. X-ray photoelectron spectroscopy (XPS) data were recorded with an ESCALAB 250 electron spectrometer using Al K irradiation. The Brunauer–Emmett–Teller (BET) surface area of the as-synthesized samples was measured using a Belsorp-max surface area detecting instrument by N_2 physisorption at 77 K. The thermogravimetry (TG) analysis of the sample was carried out with a DTG-60AH instrument with a heating rate of 20 °C min^{-1} from 25 °C to 600 °C in the air.

2.3. Electrochemical measurements

The electrochemical measurement of cyclic voltammetry (CV) and rotating disk electrode (RDE) were carried out in a three-electrode system in 0.1 M KOH at 25 °C using a CHI760E electrochemical analyzer. A glass carbon RDE with a diameter of 5 mm