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Synthesis of mesoporous $NiCo_2O_4$ fibers and their electrocatalytic activity on direct oxidation of ethanol in alkaline media

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Well-dispersed mesoporous $NiCo_2O_4$ fibers as anode catalysts for the electrooxidation of ethanol were synthesized by an easy-controlled template-free method. Their structure and morphology were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and N_2 adsorption/desorption analysis. The electrochemical oxidation of ethanol on mesoporous $NiCo_2O_4$ fibers modified glassy carbon electrode ($NiCo_2O_4$/GCE) in alkaline solutions was systematically evaluated by cyclic voltammetry (CV), double-step chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS). The $NiCo_2O_4$ materials showed typical intertwined porous nanofibrous structures with specific surface area of 54.469 $m^2 g^{-1}$ and average pore size of 13.5 nm. The $NiCo_2O_4$/GCE exhibited significantly high electrocatalytic activity with higher current density and lower onset potential compared to those of Co_3O_4 and NiO in CV measurement. The linear relationship between the ethanol concentration and the square root of scan rate indicated that diffusion of ethanol is a rate-determining step in its oxidation on mesoporous $NiCO_2O_4$ fibers. The electrochemical mechanism of ethanol oxidation on $NiCo_2O_4$/GCE was also proposed.

1. Introduction

The increasing demand for clean and high-efficiency energy has inspired considerable efforts in the development of advanced power devices [1,2], among which direct alcohol fuel cells (DAFCs) have attracted extensive attention due to their high energy conversion efficiency, abundant sources of raw materials, and good stability [3–5]. Though methanol has been widely used as the fuel for DAFCs, the problems such as its toxicity and the crossover of molecules through the proton exchange membrane restrain its application [3,6]. Among other alcohol fuels, ethanol has been considered as a promising alternative due to its lower toxicity and higher theoretical energy density compared to methanol [7,8]. In addition, ethanol can be easily produced in large quantities via the fermentation of biomass resources, which will not change the natural balance of carbon dioxide in the atmosphere in contrast to the use of fossil fuels [9]. Therefore, the direct ethanol fuel cells (DEFCs) need insightful study.

Although ethanol possesses these attractive advantages, breaking the C—C bond of ethanol for its total oxidation to CO_2 remains a major challenge in the development of high performance DEFCs. To conquer the challenge, one effective strategy is to explore electrode catalysts with high electrocatalytic activity. Traditionally, precious metals such as Pt, Pd, Ru and their alloys have exhibited high electrocatalytic activity for ethanol oxidation in acidic media [10,11]. However, the high cost, self-poisoning and poor durability of precious metals limit their large-scale application. The exploration of alkaline DEFCs offers potential alternatives as non-precious metal (NPM) catalysts [12]. In comparison with acidic media, alkaline solutions in fuel cells have impressive advantages, such as few poisoning effects [13,14] and higher efficiency in both anodic and cathodic processes [15]. More importantly, even NPM catalysts can achieve faster kinetics in both oxygen reduction reaction (ORR) and ethanol oxidation reaction (EOR) in alkaline media [16]. Therefore, the use of non-precious metals with low cost and high activity offers an effective way to significantly reduce catalyst cost without compromising the performance of alkaline DEFCs. The transition metal oxides (such as Co_3O_4 [17] and NiO [18]) are such a class of promising candidates for DEFCs applications. Their mixed valences/states are beneficial for easy ion transportation and rich redox reactions [19–21]. Among them, nickel cobaltite ($NiCo_2O_4$) has particularly drawn a great deal of interest, and considerable efforts have been devoted to its electrochemical applications as oxygen evolution reaction (OER) catalyst materials [22], high performance supercapacitors [23–25], organic synthesis electrodes [26] and

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promisingphotodetectors [27]. It has been reported that $NiCo_2O_4$ possesses a much better electronic conductivity (at least two orders of magnitude higher) and higher electrochemical activity than single nickel oxides or cobalt oxides [21,28]. Because of its high electronic conductivity, which favors the electrocatalytic performance for ethanol oxidation [29], people have great expectation for $NiCo_2O_4$ as an anode catalyst material for DEFCs. For instance, Prathap et al. [30] found urchin-like $NiCo_2O_4$ synthesized by the hydrothermal route had good electrocatalytic activity for methanol oxidation in NaOH solution; Qian et al. [31] reported that $NiCo_2O_4$ nanostructures on conductive substrates synthesized by electrodeposition exhibited enhanced electrocatalytic activity for methanol in KOH solution. However, to the best of our knowledge, its application in ethanol electrooxidation has not been reported. In addition, mesoporous electrode materials with special morphology and large surface area are conducive for improving the electrocatalytic performance of DEFCs due to the surface effect of catalysis process. The intrinsic interconnected mesopores in materials can be beneficial for efficient electrolyte diffusion, and the high specific surface area can advocate the interfacial contact between electrode and electrolyte [32]. While one-dimensional (1D) nanostructures such as nanowires and nanotubes are supposed to promote fast redox reactions and high charge/discharge rates due to the short ion and electron transport pathways [33]. As a result, it is of great significance for rational design and fabrication of electrocatalysts with 1D porous nanostructure for efficient electrocatalytic oxidation of ethanol.

In this work, mesoporous $NiCo_2O_4$ fibers were prepared by an easy-controlled template-free and large-scale synthesis method. They were used as the anode catalyst for ethanol oxidation, which showed high electrocatalytic activity and good stability.

2. Experimental

2.1. Synthesis of materials

All reagents were of analytical grade and used without further purification. All stock solutions were freshly prepared with deionized water. In a typical experiment, 9.072 g of $H_2C_2O_4{\cdot}2H_2O$ and 0.500 g of PVP were completely dissolved in a mixed solution of 50 mL ethanol and 50 mL deionized water under stirring, and followed by the addition of 4.754 g of $NiCl_2{\cdot}\ 6H_2O$ and 9.516 g of $CoCl_2{\cdot}\ 6H_2O$. When pH of the reaction solution was adjusted to 8.2 by adding $NH_3{\cdot}\ H_2O$, the reaction was conducted for 60 min under stirring at 333 K in a water bath. The stirring continued for 60 min after feeding. The precipitates were washed by water and ethanol, respectively, and dried in vacuum at 373 K for 24 h. Finally, the precipitates were annealed at 573 K in air for 1 h to obtain the mesoporous $NiCo_2O_4$ fibers.

NiO and Co_3O_4 powders were prepared by the same method according to the previous literature [34].

2.2. Characterization

The XRD patterns were recorded with an X-ray powder diffractometer (Rigaku–TTRIII) (Cu Kα, λ=0.154056 nm). The morphology of samples was characterized with scanning electron microscopy (SEM, JSM-6360LV, JEOL), transmission electron microscopy (TEM, Tecnai G2 20ST), and selected-area electron diffraction (SAED, Tecnai G2 20ST). The Brunauer-Emmett-Teller (BET) specific surface areas were calculated from the N_2 adsorption isotherms at the relative pressure range of 0.05-0.3. The Barrett–Joyner–Halenda (BJH) pore size distribution was analyzed with the adsorption branch data by using the non-local density functional theory (NLDFT) simulations.

2.3. Preparation of modified electrode

The glassy carbon electrode (GCE, 5 mm diameter) was mechanically polished with 50 nm gamma alumina powder, rinsed thoroughly with deionized water, and dried at room temperature. The mesoporous $NiCo_2O_4$ fibers (50 mg) were firstly dispersed in deionized water (2 mL), and the mixture (4 μL) was dropped on the surface of GCE and air dried. Nafion solution (5 wt. %, 2 μL) was covered onto the surface of $NiCo_2O_4$ modified glassy carbon electrode ($NiCo_2O_4$/GCE). NiO modified glassy carbon electrode (NiO/GCE) and Co_3O_4 modified glassy carbon electrode (Co_3O_4/GCE) were obtained by the same method.

2.4. Electrochemical measurements

Electrochemical measurements were carried out with an electrochemical workstation (CHI660B) using a three-electrode setup. A saturated calomel electrode (SCE), a Pt electrode and a modified glassy carbon electrode were used as the reference, counter and working electrodes, respectively. All studies were performed at 298 ± 2 K.

3. Results and Discussion

3.1. Physical characterization of as-prepared mesoporous $NiCo_2O_4$ fibers

Fig. 1 shows X-ray diffraction (XRD) patterns of the as-prepared $NiCo_2O_4$, NiO and Co_3O_4. As seen in the XRD patterns of NiO, the diffraction peaks at 2θ of 37.2°, 43.3°, 62.8°, 75.3° and 79.3°correspond well to the (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2) facets of NiO (JCPDS No. 73-1523). The XRD patterns of Co_3O_4 are in agreement with the standard Co_3O_4 (JCPDS No. 43-1003), without reflection peaks from other crystallized phases observed. For the XRD patterns of $NiCo_2O_4$, the observed peaks can be well indexed with the face-centered cubic spinel $NiCo_2O_4$ (JCPDS No. 73-1702). Moreover, it is noted that $NiCo_2O_4$ and Co_3O_4 have similar patterns. The cubic lattice parameter α of $NiCo_2O_4$ from the (3 1 1) plane is calculated to be 0.8115 nm. This value is in accordance with the theoretical value of 0.8114 nm, and much larger than the theoretical value for Co_3O_4 (0.8065 nm), thereby indicating the high phase purity of $NiCo_2O_4$ product. The cubic lattice parameter α for NiO and Co_3O_4 were calculated to be 0.4191 nm and 0.8090 nm, matching the theoretical values (0.4178 nm for NiO and 0.8065 nm for Co_3O_4).

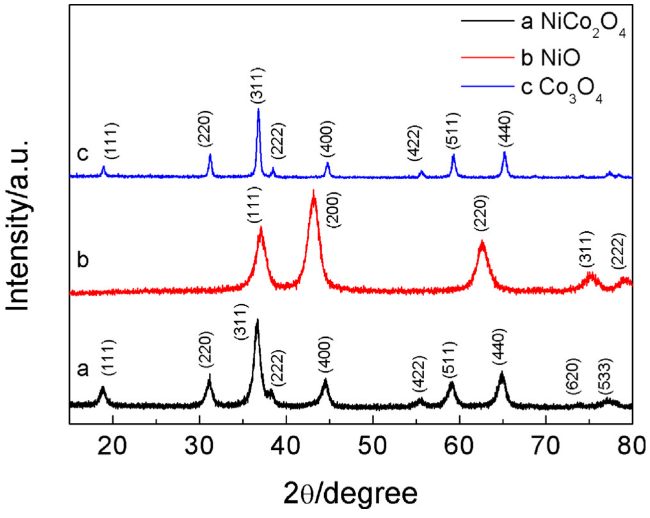

Fig. 1. XRD patterns of (a) $NiCo_2O_4$, (b) NiO, and (c) Co_3O_4.