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Effect of cobalt precursors on Co_3O_4 anodic catalyst for a membrane-free direct borohydride fuel cell

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ABSTRACT

The fuel discharging efficiency of direct borohydride fuel cell (DBFC) depends on both the anodic catalyst activity and borohydride hydrolysis. In this paper, Co_3O_4 anodic catalysts prepared from different cobalt sources used in DBFC have been investigated. It showed that the catalytic performance of Co_3O_4 was associated with its microstructure that relied on the precursor. The maximum power densities obtained was 40, 62 and 28 mW cm^{-2} of DBFC with Co_3O_4 catalyzed anode from $CoCl_2$ (marked DBFC-A), $Co(NO_3)_2$ (marked DBFC-B) and $Co(CH_3COO)_2$ (marked DBFC-C), respectively. The Co_3O_4-A has the highest number of electron transfer ($n = 7.06$) which is close to the theoretical value ($n = 8$), and DBFC-A showed good voltage stability with specific capacity of 720 mAh.g^{-1}. A rapid voltage attenuation occurred in DBFC-B with the specific capacity of 330 mAh.g^{-1} because Co_3O_4 from $Co(NO_3)_2$ has the higher catalytic activity for both borohydride oxidation reaction (BOR) and hydrolysis which lead to the lower fuel utilization efficiency.

1. Introduction

Many problems, such as the fossil energy shortage, haze weather, increasingly rapid growth of electricity demand of mobile devices, force people to look for new alternative energy and to explore the effective way of energy conversion. Fuel cell is one of the most promising devices for environmental friendly power generation by converting chemical energy directly into electrical energy without limitation of the Carnot efficiency. Borohydride is one of energetic materials, it can be catalyzed to produce hydrogen as fuel in acidic and neutral solution, and it can be oxidized to generate electrons directly in alkaline solution. Based on the alkaline mechanism, direct borohydride fuel cell (DBFC) [1–10], a liquid fuel cell with low operating temperature, appeared, and its working mechanism is as follows:

Anode reaction:

$$BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^- \quad E_a^0 = -1.24V vs.SHE \tag{1}$$

Cathode reaction:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad E_c^0 = 0.4V vs.SHE \tag{2}$$

Overall reaction:

$$BH_4^- + 2O_2 \rightarrow BO_2^- + 2H_2O \quad E^0 = 1.64V vs.SHE \tag{3}$$

Hydrolysis reaction(side reaction):

$$BH_4^- + 2H_2O \rightarrow 4H_2 + BO_2^- \tag{4}$$

The advantages of DBFC, such as high theoretical open-circuit voltage (OCV), high H-capacity and environmental safety, are considerable. To be honest, like the other fuel cells, there is still a great distance away from the actual application. Through a great deal of efforts, the problem of high cost and borohydride crossover has been solved with non-noble catalysts development and membrane-free cell structure [6,11,12]utilization. However, how to improve the fuel conversion efficiency and power density become the key problems at present. In order to solve problems mentioned above, anodic behavior of the borohydride oxidation (as reaction (1)) and borohydride hydrolysis (as reaction (4)) must be investigated. Ultimately, these decide the properties of anodic catalyst.

As reported, 8e transfer of reaction (1) could be achieved by Au catalyst only with 100% fuel conversion efficiency but a very low power density. Recently, hydrogen storage alloys [13,14], noble metals and their alloys [4,5,15–24], and metal-oxide composite

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materials [1,6,25], and Co-based catalysts [6,9,12,26–28] have been studied due to their high activity for borohydride oxidation reaction (BOR). Li's [27] and yang's [12] researches showed that the CoO could be used as anode catalyst for DBFC, and the amorphous Co-B can improve the kinetics performance effectively and the Au@Co-B improved about 80% compared with the DBFC which employed pure Au as anode catalyst [6].

Here, Co_3O_4 was firstly applied to BOR and the effect of cobalt precursors on Co_3O_4 anodic catalyst has been investigated.

2. Experimental details

2.1. Preparation of Co_3O_4

All the chemicals of AR-grade were purchased from Aladdin reagent co., LTD. The Co_3O_4 samples were prepared by the homogeneous precipitation method. Added $NH_3 \cdot H_2O$ drop-wise to 1 M $CoCl_2 \cdot 6H_2O$ solution under vigorous stirring at 30 °C, the pH value of the suspension after precipitation reaction was monitored to 8.5–9, until the precipitate color become green. After a continuous stirring for 30 min, the obtained precipitate was filtered and washed with deionized water and alcohol to remove the unreacted chemicals. After drying at 80 °C for 24 h, the precipitate was heated at 275 °C with a ramp of 5 $°C \cdot min^{-1}$ for 2 h. The object product of Co_3O_4 was obtained which was mark Co_3O_4-A sample. The procedures of Co_3O_4 preparation from cobalt sources of $Co(NO_3)_2 \cdot 6H_2O$ and $Co(CH_3COO)_2 \cdot 4H_2O$ were as same as Co_3O_4-A sample with different calcination temperature, noted as 220 °C and 300 °C, respectively. The obtained products were marked Co_3O_4-B and Co_3O_4-C.

2.2. Characterization techniques

Phase compositions of the prepared Co_3O_4 samples were characterized by an X-ray diffractometer (XRD-6000,Shimadzu, Japan) with CuKα radiation in the 2θ range of 10–80°. XPS spectra were obtained from a Thermo Fisher Scientific XPS instrument (K-Alpha, America). Morphology of the prepared Co_3O_4 samples were tested by field emission scanning electron microscope (FESEM, Zeiss supra55,Germany) operating at 5–10 kV.

2.3. Preparation of electrodes and the DBFC

The $LaNiO_3$ catalyzed cathode was prepared by method of our previous work [11]. To prepare the anode, Co_3O_4 was mixed together with acetylene black (5 wt.%) and polyvinyl alcohol as adhesive, then the mixture was smeared onto a Ni-foam. After drying at 80 °C in vacuum for 2 h, the anode was compacted by 5 MPa pressure. In order to activate the anode, it was pretreated in the 6 M KOH and 0.8 M KBH_4 aqueous solutions for 24 h. The loading mass of Co_3O_4 is 100 mg cm^{-2}. In this study, we made a DBFC in which the fuel was stored in an attached fuel tank (18 mL) and the cathode worked by air-breathing without any auxiliary facilities. The electrodes were placed with a distance of 1 mm to prevent short-circuits, without using any Nafion membrane or polymer electrolyte membrane.

2.4. Test equipments and methods

As testing, the fuel solution consisted of KOH and KBH_4 was added to the fuel tank, and the source of oxygen was obtained from air through the gas diffusion layer.

The line sweep voltammetry (LSV) and chronoamperometry tests were employed by using a computer controlled CHI920D electrochemistry workstation (CH Instrument, Inc., USA). The discharging performances of the DBFCs were measured by using a battery testing system (from Neware Technology Limited, Shenzhen, China). In order to evaluate the performances of the electrodes, the *V*–*I* characteristic curves for the cathode were generated using a conventional three-electrode electrochemical system consisting of the gas diffusion electrode as working, the Pt wire as counter and the Hg/HgO as reference electrodes. All the tests were operated at ambient temperature.

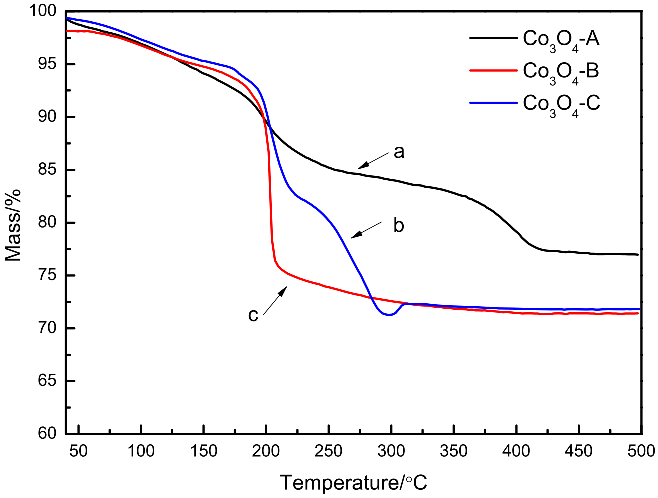

Fig. 1. TGA profiles of the precursor of Co_3O_4.

3. Results and discussion

3.1. Analysis of the precursor of Co_3O_4

Thermogravimetric analysis (TGA) was carried out to investigate the thermal behavior of the different cobalt precursors which are $CoCl_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and $Co(CH_3COO)_2 \cdot 4H_2O$. The TGA curves of the precursors are shown in Fig. 1. It can be seen that there are three distinct weight loss stages. In curve (a), the first weight loss of about 7.2% occurs at 30–175 °C, which was ascribed to the evaporation of water. A weight loss was about 8% in the second stage corresponds to the thermal decomposition of $Co(OH)_2$

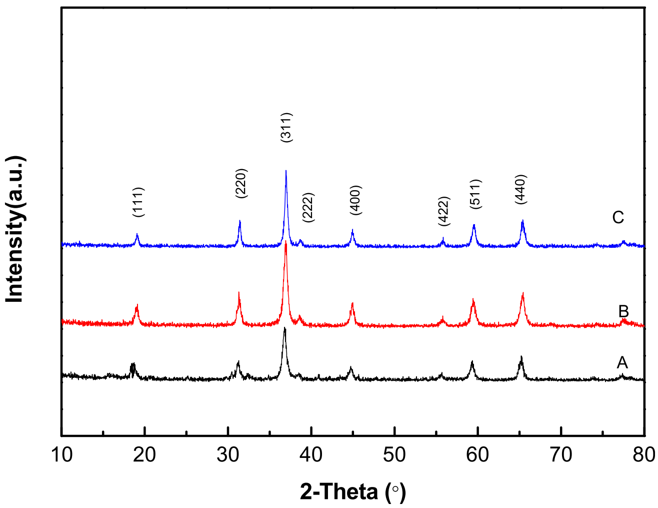

Fig. 2. XRD patterns of as-prepared Co_3O_4 samples.