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Ultrafine amorphous Co–W–B alloy as the anode catalyst for a direct borohydride fuel cell

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ABSTRACT

The ultrafine amorphous Co–W–B alloy has been synthesized by chemical reduction and used as anode catalyst in direct borohydride fuel cell. The results show that the maximum power output of the cell is 101 mW cm^{-2} at 15 °C, and the essential power density of this material can be up to 350 mW cm^{-2} at 15 °C and 500 mW cm^{-2} at 60 °C, respectively. The cell has also a good durability, with no attenuation observed after one week of operation.

1. Introduction

Fuel cells, which can convert chemical energy into electrical energy with a high efficiency and low/zero-emission, are considered as promising power sources. It widely used in the field, such as mobile phones, portable computers, automobiles and power generators. Among various fuel cells, direct borohydride fuel cell (DBFC) which use KBH_4 or $NaBH_4$ aqueous solution as fuel [1] is one of the most exciting energy technologies. Compared with other liquid fuel cells, DBFC has many advantages [2–4] such as high theoretical open cell voltage (OCV) (1.64 V), high energy density (9300 Wh kg^{-1}), and low toxicity of borohydride. However, its development and commercialization is limited by some key issues like high cost.

Platinum or platinum-based catalysts show good catalytic activity toward the electrochemical oxidation reaction, and are wildly employed in DBFC. However the platinum resources are extremely limited [5], giving rise to the main technological obstacles in the development of DBFC. Lots of researchers have been therefore interested in exploring lower-cost substitutes, and have made some progresses. For examples, some transition metals (Ni and Cu) [6,7] and hydrogen storage alloys (AB_5- and AB_2-type alloys) [8–10] have been successful alternative platinum as anode in DBFCs. More recently, much effort has been engaged in developing binary alloy [3]. Such material is particularly important in the field of catalysts attributing to better catalytic properties than single component. For example, Geng et al. [11] prepared carbon-supported Ni and Ni–Pt anodic catalyst. Electrochemical measurements showed that the binary alloy Ni–Pt has a better electrocatalytic activity and stability than pure metal Ni catalyst [11]. Feng et al. [12] studied Ag and Ag–Ni alloy as anode catalyst and found that Ag–Ni alloy exhibited a higher

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discharge voltage and larger capacity than Ag. In our previous studies [13], we found as well that the amorphous CoB alloy for catalytic oxidation reaction of BH_4^- prepared by the combination of 3d transition metals Co with boron exhibited excellent electrochemical performance for DBFC.

Based on our previous works, in this study, we explored the performance of multi-metal alloys materials and found by introducing W into the binary CoB alloy that the catalytic activity of the CoB is significantly improved.

2. Experimental

2.1. Catalyst preparation

The ultrafine amorphous Co–W–B catalyst was synthesized by chemical reduction of cobalt chloride ($CoCl_2$) and sodium tungstate (Na_2WO_4) with potassium borohydride solution [14]. The different volume of $CoCl_2$ (0.2 mol L^{-1}) and Na_2WO_4 (0.2 mol L^{-1}) solutions were mixed together to adjust the tungsten content in samples. Then 2.0 mol L^{-1} KBH_4/0.2 mol L^{-1} KOH solution was added dropwise into the mixed solution at magnetic stirring. The B: (Co + W) molar ratio was 3.0. The stirring needs to be held for 1 h without stop after the addition of potassium borohydride to release hydrogen. The resulting black precipitate was filtrated and washed with distilled water to neutrality, cut off from air by absolute alcohol and finally dried under vacuum at 60 °C for 12 h. The cathode catalyst, perovskite-type oxide ($LaNi_{0.9}Ru_{0.1}O_3$) was prepared following the sol–gel method described by previous paper [15]. Lanthanum nitrate ($La(NO_3)_3$ $6H_2O$), nickel nitrate ($Ni(NO_3)_2$ $6H_2O$), ruthenium chloride ($RuCl_3$ nH_20), citric acid ($C_6H_8O_7$ H_2O), and ammonia water (NH_3 H_2O) (25–28 wt.%) were used as raw materials. All the reagents are of analytical grade in purity (Beijing Jinkemei chemical product co. ltd.).

2.2. Catalyst characterization

The particle size and morphology of the samples were observed by transmission electron microscopy (TEM). The structure of the Co–W–B powders was investigated with an X-ray diffractometer (D/MAX-3A, Japan) using a Cu Ka ($\lambda = 1.5444$ Å) source. The elemental composition of the sample was analyzed by energy-dispersive X-ray spectroscopy (EDX).

2.3. Electrodes preparation

To prepare the anode, Co–W–B powders (78 wt.%) were mixed together with 30% polytetrafluoroethylene (PTFE) solution (22 wt.%). The mixture was smeared onto a 1 cm × 1 cm Ni-foam sheet (thickness = 1.7 mm, porosity > 95%). An experiment [16] with a blank sample without catalyst on Ni-foam proved that Ni-foam has no catalytic activity for BH_4^-. The electrode is dried at 80 °C under vacuum for 2 h, and was pressed under 3 MPa. The mass loading in the anode was 70 mg cm^{-2}.

The cathode has a sandwich construction consisting of a gas diffusion layer, an active layer and a current accumulating matrix. The active layer was prepared by mixing 30 wt.% $LaNi_{0.9}Ru_{0.1}O_3$ and 45 wt.% carbon nanotubes with a 25 wt.% polytetrafluoroethylene (PTFE) emulsion and then coated onto a Ni-foam. The mass loading in the cathode was 7.5 mg cm^{-2}. The gas diffusion layer was prepared by mixing 60 wt.% acetylene black and 40 wt.% PTFE with ethanol and rolled into 0.3 mm thick film. The three-layer electrode was finished by pressing the coated Ni-foam and the gas diffusion layer at pressure of 3 MPa into a sheet with thickness of 0.6 mm.

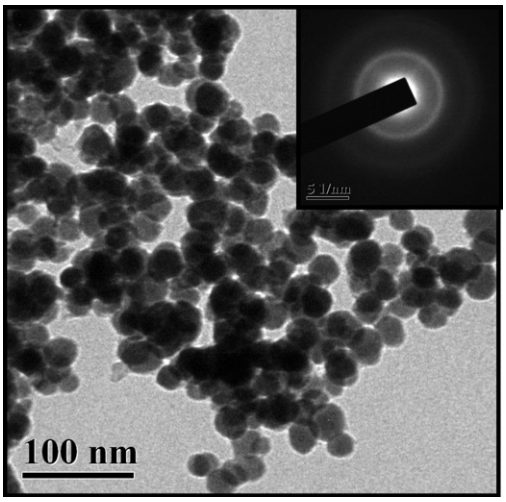

Fig. 1 – TEM images of the Co–W–B catalyst.

2.4. The cell performances evaluation

The cell performances were measured by a battery testing system (from Neware Technology Limited, Shenzhen, China). In the cell test system, the anode was placed inside of a container, the cathode was fixed on a square window of the container wall, and the area of the window was 1 cm^2. The gas diffusion layer of the cathode was exposed to air, whereas the active layer was in contact with the electrolyte. The anode was 2 cm away from the cathode. The electrolyte fuel was 0.8 M KBH_4–6 M KOH. And the structure of the DBFC has been described in our previous paper [16].

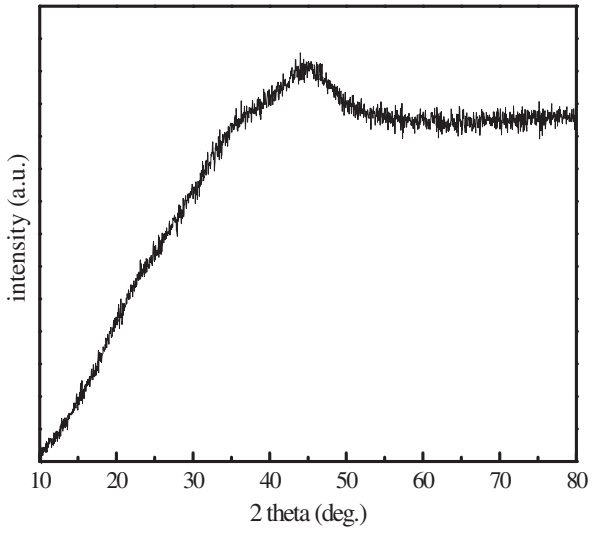

Fig. 2 – The XRD pattern of the Co–W–B catalyst.