



Short communication

Investigation of amorphous CoB alloy as the anode catalyst for a direct borohydride fuel cell

Sai Li^a, Xiaodong Yang^a, Haiyan Zhu^b, Yuanzhen Chen^a, Yongning Liu^{a,*}^a State Key Laboratory for Mechanical Behavior of Materials, School of Materials Science and Eng., Xi'an Jiaotong University, Xi'an 710049, PR China^b Department of Chemistry and Chemical Engineering, Weinan Teacher's University, Weinan 714000, PR China

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ABSTRACT

Co-B amorphous alloy powders have been synthesized by chemical reduction of cobalt chloride with potassium borohydride in an aqueous solution. We find that this alloy can be used as an anode catalyst for a direct borohydride fuel cell (DBFC). This catalyst exhibits excellent electrocatalytic activity. An essential power output of 220 mW cm⁻² has been achieved at 15 °C, and a life test last for 160 h with no attenuation has been observed. The amorphous structure of the CoB alloy is still stable after the life test.

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1. Introduction

Direct borohydride fuel cells (DBFCs) using a borohydride (KBH₄ or NaBH₄) aqueous solution as fuel have been drawing increasing attention because of their high energy density, the low toxicity of borohydride, their good power performance, and the feasibility of using non-noble metals as both the anode and cathode catalysts [1–3].

A DBFC with excellent performance involves high catalysis efficiency at both the anode and the cathode. In the past few decades, many types of materials, such as noble metals (platinum, palladium, and gold) [4–6], transition metals (nickel and copper) [7] and rare earth hydrogen storage alloys (AB₅- and AB₂-type alloys) [8–10], have been developed and successfully applied as anode catalysts in DBFCs. However, electrocatalyst selection is always important. Recently, a new type of material, transition metal (TM) borides, has attracted considerable attention for its use as the electrode material in several types of batteries [11,12]. In the last few years, considerable progress has been made on the applications of Co-based borides (Co-B). For instance, Wang et al. [13] reported that ultra-fine amorphous alloy particles of Co-B have a discharge capacity of approximately 300 mA h g⁻¹ when used as the electrode material for NiMH batteries and that they show excellent reversibility. Liu et al. [14] demonstrated that the Co_xB series alloys showed excellent cycling stability; the capacity retentions were all above 93%

after the 100th cycle. Furthermore, some novel Co-based borides, such as Co-Mo-B [15], have been used successfully as battery-active materials for alkaline batteries. These studies indicate that the TM borides can be used as catalysts in DBFCs. In our previous studies [16], we discovered that an amorphous CoB alloy was formed during fuel cell operation when using CoO as the anodic catalyst in a DBFC. To further confirm the catalytic action of CoB alloys, amorphous alloy powders of CoB were directly synthesized in this study and were used as anode catalysts in a DBFC. Material structure and fuel cell performance were also investigated.

2. Experimental

2.1. Catalyst preparation

All the reagents were of analytical grade purity (Beijing Jinke-me Chemical Product Co., Ltd.). Amorphous CoB alloy powders were synthesized by chemical reduction of cobalt chloride with a potassium borohydride solution [17]. A typical experimental procedure was as follows: the potassium borohydride aqueous solution (2.0 mol L⁻¹, 70 mL) was stabilized by 0.2 mol L⁻¹ of potassium hydroxide. The potassium borohydride solution was then added dropwise into cobalt chloride solution (0.1 mol L⁻¹, 100 mL) with magnetic stirring. The stirring continued for 1 h after the addition of potassium borohydride to release the hydrogen. Next, the resulting black precipitate was filtrated and washed with distilled water to remove the reaction residues, and it was then cut off from air by absolute alcohol (EtOH). Finally, it was dried under vacuum at 60 °C for 12 h. The cathode catalyst, perovskite-type oxide (LaCoO₃), was

* Corresponding author. Tel.: +86 29 8266 4602; fax: +86 29 8266 3453.
E-mail address: ynliu@mail.xjtu.edu.cn (Y. Liu).

prepared following the sol–gel method, as described in a previous paper [18]. Lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$), and ammonia water ($\text{NH}_3 \cdot \text{H}_2\text{O}$) were used as the raw materials.

2.2. Catalyst characterization

The catalyst structure of the CoB powders was investigated with an X-ray diffractometer (XRD) (D/MAX-3A, Japan) using a $\text{Cu K}\alpha$ ($\lambda = 1.5444 \text{ \AA}$) source. The particle size and the morphology of the samples were observed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The elemental composition of CoB was analyzed with energy-dispersive X-ray spectroscopy (EDX).

2.3. Electrode preparation

To prepare the anode, CoB powders (97 wt.%) were mixed together with 30% polytetrafluoroethylene (PTFE) solution (3 wt.%) and then smeared onto a $1 \text{ cm} \times 1 \text{ cm}$ Ni-foam sheet (thickness = 1.7 mm, porosity > 95%). An experiment [16] using a blank sample in which there was no catalyst except for the Ni-foam proved that Ni-foam had no catalytic activity for BH_4^- . After drying at 80°C under vacuum for 2 h, the electrode was pressed with a pressure of 3 MPa. The mass loading of CoB in the anode was 70 mg cm^{-2} .

The cathode was 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.% LaCoO_3 and 45 wt.% activated carbon with a 25 wt.% PTFE emulsion and then coated this mixture onto Ni-foam. The gas diffusion layer was prepared by mixing 60 wt.% acetylene black (with surface area $2500 \text{ m}^2 \text{ g}^{-1}$) and 40 wt.% PTFE with ethanol and rolling this mixture into a 0.3 mm thick film. The three-layer gas electrode was finished by pressing the coated Ni-foam and the gas diffusion layer at a pressure of 3 MPa into a sheet with a thickness of 0.6 mm. The mass loading of LaCoO_3 in the cathode was 7.5 mg cm^{-2} .

2.4. Cell performance evaluation

The cell performances were measured by a battery testing system (from Neware Technology Limited, Shenzhen, China). The structure of this DBFC has been described in a previous paper of ours [16]. The anode was placed inside a container, the cathode was sandwiched 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.

3. Results and discussion

3.1. Catalyst characterization

The XRD patterns of the prepared catalyst are illustrated in Fig. 1. In Fig. 1, only a broad peak appears at approximately $2\theta = 45^\circ$. This wide, diffuse peak indicates that this sample's crystalline structure is amorphous. Fig. 2 shows the morphology of the experimental materials. As seen in the SEM micrograph, the CoB alloy particles presented in the form of globular particles and were distributed uniformly, with an average particle size of approximately 50 nm. The morphology of the catalyst was also observed via TEM. The TEM image and corresponding selected area diffraction (SAD) pattern are shown in Fig. 3. The TEM image reconfirmed that the morphology of CoB is generally spherical and that the mean particle size is approximately 50 nm. In addition, the diffused ring in the SAD

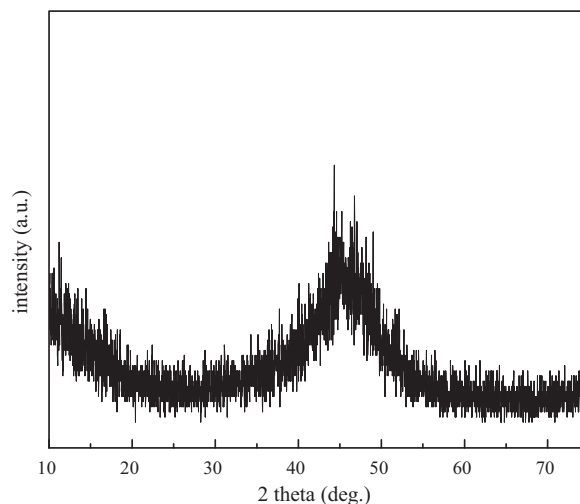


Fig. 1. The XRD pattern of the CoB alloy catalyst.

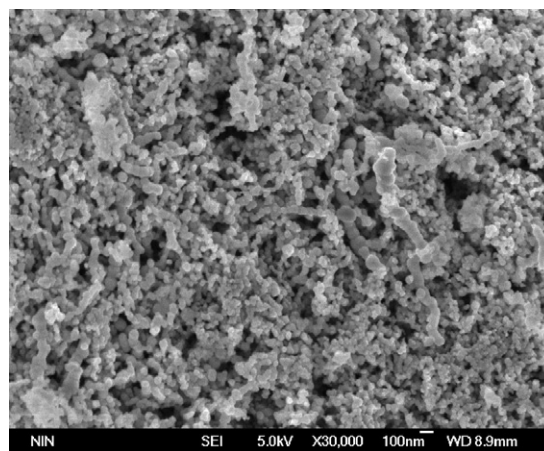


Fig. 2. SEM image of the CoB alloy catalyst.

pattern reconfirmed that the alloy powders are amorphous. Fig. 4 shows the EDX for the samples corresponding to a selected zone in the powder sample indicated in the inset. The EDX analysis revealed that the Co/B atomic ratio is 1.3:1, nearly 1:1.

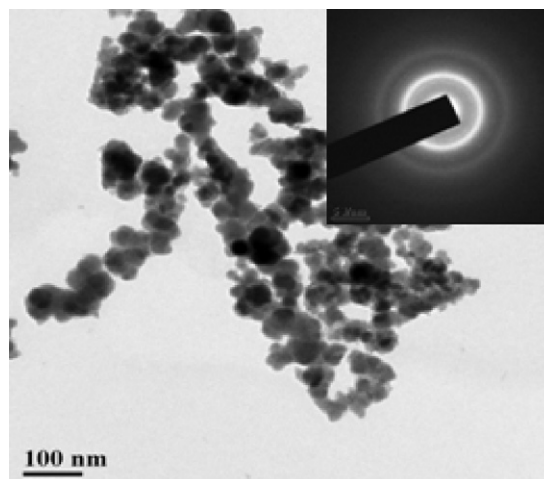


Fig. 3. TEM image of the CoB alloy catalyst.

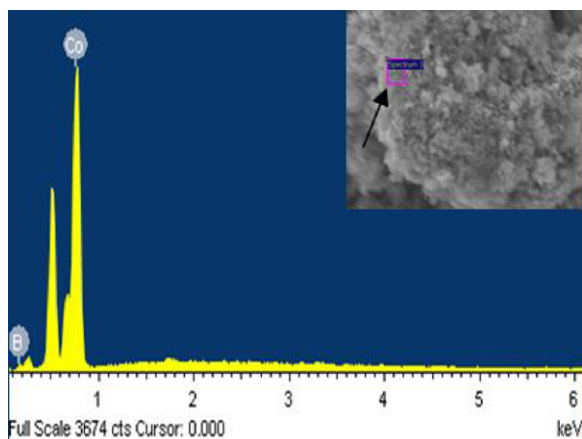


Fig. 4. Energy-dispersive X-ray spectroscopy of the CoB alloy catalyst.

3.2. Cell performance evaluation

The polarization curves of the CoB anode and the LaCoO_3 cathode are shown in Fig. 5. In this figure, the potential variation between the anode and cathode clearly indicates that the electrochemical dynamics of the cathode are inferior to those of the anode. For example, when the current density changes from 0 to 100 mA cm^{-2} , the cathode potential decreases from 0 to -0.34 V and the anode potential increases from -1.1 to -1.08 V , suggesting that the cathode polarization significantly influences the cell output voltage and is the constraining factor. Based on this analysis, we reduced the anode electrode area and kept the cathode area constant during an investigation of the anode materials. In other words, we enlarged the cathode to meet the needs of the anode. Fig. 6 shows the polarization curves and the corresponding power densities of the tested cells that were assembled with anodes of different sizes and cathodes of constant size. Different power densities were obtained, depending on the size of the anode electrode area. The highest power density, 220 mW cm^{-2} , was achieved at 15°C when the anode size was 0.25 cm^2 . This value represents the essential or maximum power that the anode materials can output. The results also demonstrate that the cathode performance restricted the cell performance. When the anode and cathode were

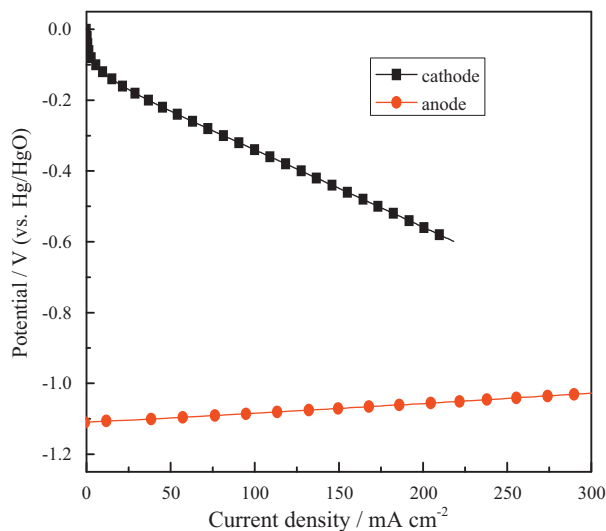


Fig. 5. Comparison of the polarization curves between the anode and the cathode. Anode: the CoB loading is 70 mg cm^{-2} ; the anolyte is $0.8 \text{ M KBH}_4\text{-6 M KOH}$. Cathode: LaCoO_3 and the loading is 7.5 mg cm^{-2} ; electrolyte is 6 M KOH .

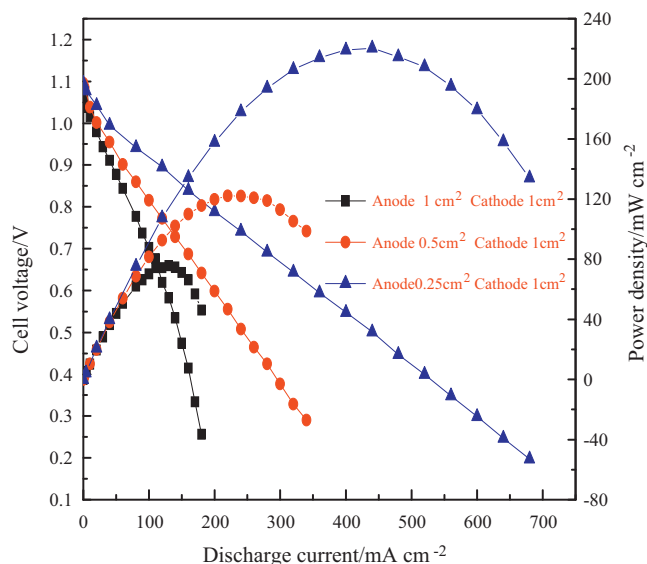


Fig. 6. Performances of the DBFCs using different anode areas (CoB). The cathode (LaCoO_3) area is 1 cm^2 . Anode loading: 1 cm^2 is 70 mg cm^{-2} , 0.5 cm^2 is 35 mg cm^{-2} and 0.25 cm^2 is 17.5 mg cm^{-2} . Cathode loading: 7.5 mg cm^{-2} . The electrolyte fuel is $0.8 \text{ M KBH}_4\text{-6 M KOH}$, and the temperature is 15°C .

the same size, the peak power density was only 75 mW cm^{-2} at 15°C .

Fig. 7 compares the DBFC performance of our experiment, which employed CoB as the anode, with values from the literature, obtained using Ni + Pd/C [19] and Pt/C [20] as the anode and Pt/C as both the anode and cathode [20]. This figure shows that a relatively high power density (93 mW cm^{-2}) can be achieved using CoB as the anode material. According to the several studies, amorphous materials have much more structural distortion and thus yield more active sites than crystalline materials [21,22]. Therefore, the excellent cell performance should be attributed to the amorphous structure of the CoB alloy.

Cell performance stability is another important aspect. The DBFC short-term stability was tested by monitoring the voltage changes in the cell during galvanostatic discharge. Fig. 8 shows the changes in the cell voltage at a constant current discharge of 20 mA cm^{-2} , which continued for approximately 160 h at room temperature. As

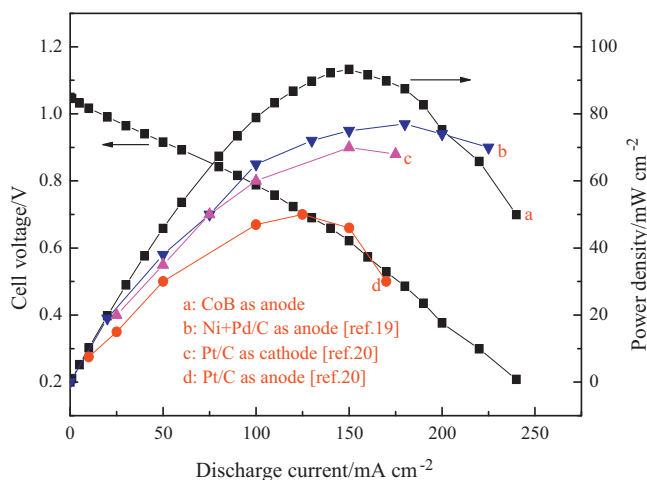


Fig. 7. The performance of the DBFCs. (a) CoB as the anode (loading was 70 mg cm^{-2}), LaCoO_3 as the cathode (loading was 7.5 mg cm^{-2}); the electrolyte fuel was $0.8 \text{ M KBH}_4\text{-6 M KOH}$, and the temperature was 30°C . (b) Ni + Pd/C [19] as the anode, Pt/C as the cathode. (c) Pt/C [20] as the cathode, Au/C as the anode. (d) Pt/C [20] as both the anode and the cathode.

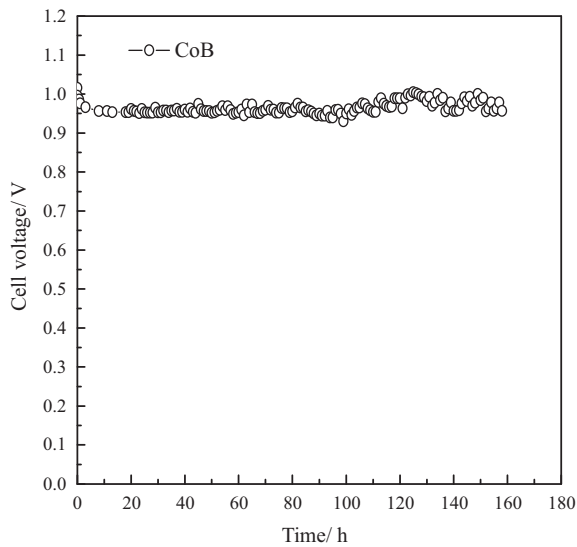


Fig. 8. A stability test of the DBFC using a CoB anode operating at a current density of 20 mA cm^{-2} at room temperature. Anode: the CoB loading is 70 mg cm^{-2} . Cathode: the LaCoO_3 loading is 7.5 mg cm^{-2} . The electrolyte fuel is $0.8 \text{ M KBH}_4\text{--}6 \text{ M KOH}$.

shown in Fig. 8, despite some slight fluctuations, attenuation was not observed after 160 h, suggesting that the cell using CoB as the anode catalyst had good performance stability.

3.3. CoB structure after cell operation

In order to understand the function of CoB as an anode catalyst, the microstructure and elemental composition of CoB after operation were examined using XRD, SEM, and EDX. The examination using XRD (see Fig. 9) revealed that there were no other diffraction peaks except for that of the Ni-foam, suggesting that the CoB was still in the amorphous state. This finding is an indication that the catalyst can maintain a steady-state. At the same time, the original spherical shape remained, as shown in Fig. 10. Moreover, Fig. 11 shows that, after the life test for 160 h, the Co/B atomic ratio was still approximately 1:1. The C, O, and F (see Fig. 11) are from the PTFE, which was used as a binder, and from residual EtOH used in the sample washing after the measurement. The EDX analysis further confirmed the stability of CoB as a catalyst.

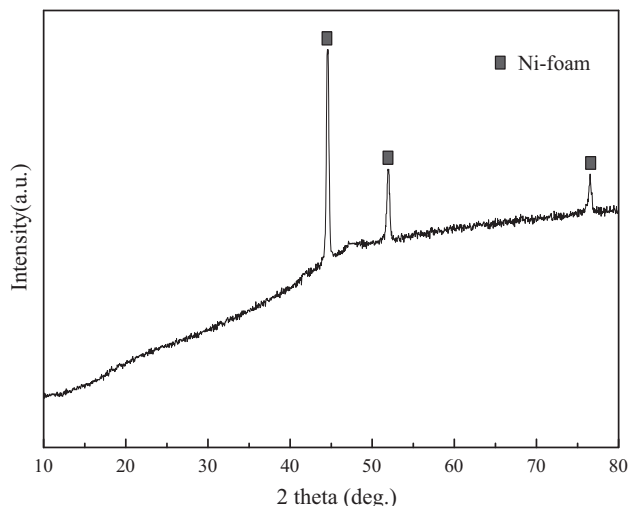


Fig. 9. XRD pattern of the CoB after operation.

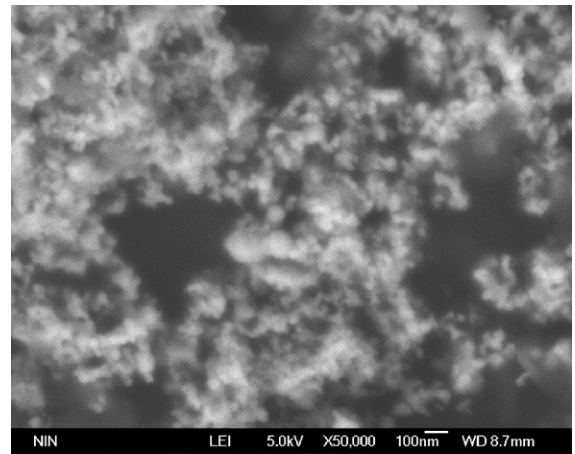


Fig. 10. SEM image of the CoB alloy catalyst after the life test for 160 h.

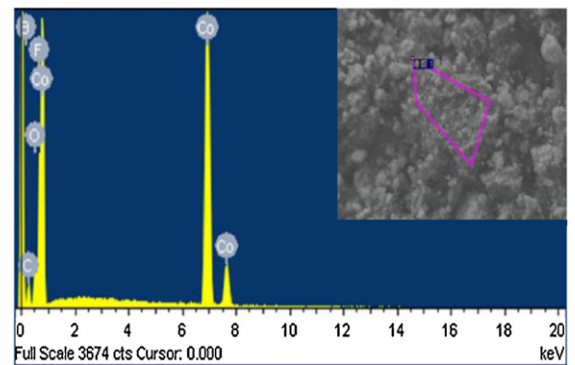


Fig. 11. Energy-dispersive X-ray spectroscopy of the CoB after the life test for 160 h.

4. Conclusions

In summary, we prepared amorphous CoB powders and studied their electrochemical properties for possible use as the anode catalyst in a DBFC. Our experiments indicated that CoB possesses exceptional electrochemical activities compared with some other materials. A peak power density of 93 mW cm^{-2} was obtained at 30°C for equal areas at both electrodes. An essential power output of 220 mW cm^{-2} was achieved with a 0.25 cm^2 anode area. The DBFC maintained a relatively stable performance for up to approximately 160 h. It was found that the amorphous CoB alloy maintained a steady state after operation. It is possible that the amorphous TM borides may be promising high-performance non-precious-metal anode materials for DBFCs.

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