



Short communication

LaNi_{4.5}Al_{0.5} alloy doped with Au used as anodic materials in a borohydride fuel cellZhenzhen Yang, Lianbang Wang^{*,1}, Yunfang Gao, Xinbiao Mao, Chun-An Ma^{*,1}

State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, College of Chemical Engineering and Material Sciences, Zhejiang University of Technology, Hangzhou City, Zhejiang 310032, PR China

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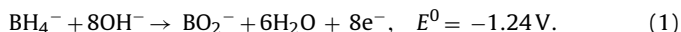
ABSTRACT

Fuel cells using borohydride as the fuel have received much attention because of their high thermodynamic cell voltage. Using rare-earth hydrogen storage alloys as the anodic catalyst materials instead of noble metals showed high catalytic activity both in the electrochemical oxidation and the hydrolysis of borohydride. In this work, we doped Au to modify the surface structure of LaNi_{4.5}Al_{0.5} alloy by a self-reduction reaction method. The surface of the alloy particles was evenly covered with Au after treatment. The largest discharge current density increased from about 150 mA cm⁻² (discharge to -0.6 V versus Hg/HgO electrode) with the parent alloy to 250 mA cm⁻² with the Au-doped alloy. This finding suggested that the electrochemical catalytic activity of the alloy was enhanced after modification with Au. Fuel utilization also increased after modification with Au.

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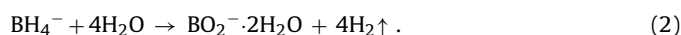
1. Introduction

Fuel cells are attractive alternative energy conversion devices because of their high efficiency and low pollution. Some fuel cells, such as the proton exchange membrane fuel cell, the alkaline fuel cell, and the phosphoric acid fuel cell, require gaseous hydrogen as the fuel. However, the direct borohydride fuel cell is an electrochemical system in which the chemical energy of borohydride is converted directly into electrical energy. Such a fuel cell was first proposed in the early 1960s [1,2] by Indig, Snyder and Jasinski, who reported that the direct electricity generation from the borohydride ion could be practical. The reactions are based on the following equation [3–5]:



The direct anodic oxidation of borohydride provides a more negative potential and higher cell voltage than that of a gaseous hydrogen fuel cell. The storage and transportation of borohydride can be carried out in a solid state or liquid state, which is much more convenient than the gaseous and liquid states of hydrogen. Hydrolysis, an unwanted reaction, occurs to some extent in all BH₄⁻

solutions and generates hydrogen gas, as described by the following equation [6–8]:



Effective use of the BH₄⁻ faradaic capacity requires that the electrochemical oxidation rates should be much higher than the rate of the competitive side reaction. Li et al. [9,10] and Lee et al. [11] reported that Zr–Ni alloys were used as the anodic materials. A complete borohydride fuel cell has been developed and showed high power density. Choudhury et al. [12] developed a fuel cell using sodium borohydride as the fuel, hydrogen peroxide as the oxidant, and various AB₅ and AB₂ alloys as the anodic materials. A peak powder density of approximately 150 mW cm⁻² at a cell voltage of 540 mV could be achieved under optimized conditions at 70 °C. Amendola et al. [13] developed a borohydride fuel cell using Au–Pt alloy electroplated on carbon cloth as the anode and a commercial gas diffusion electrode as the cathode. The number of electrons used was around seven of a total of eight electrons calculated in Eq. (1). Gyenge [3] studied the electrochemical oxidation of BH₄⁻ on Pt and Au electrodes by various electrochemical methods and found that adding thiourea could improve the BH₄⁻ utilization efficiency and coulombic efficiency of direct borohydride fuel cells because adding thiourea minimized the catalytic hydrolysis of BH₄⁻ on the Pt electrode.

To restrain the hydrolysis and improve the utilization efficiency of BH₄⁻, we wanted to explore the possibility that AB₅-type hydrogen storage alloy doped with noble metals could be used as the

* Corresponding authors. Tel.: +86 571 88320611; fax: +86 571 88320813.
E-mail addresses: wanglb99@zjut.edu.cn (L. Wang), science@zjut.edu.cn (C.-A. Ma).

¹ ISE member.

anodic material in a borohydride fuel cell. Using Au as the catalyst could hasten the eight-electron reaction [13]. In this work, we doped Au to modify the surface structure of $\text{LaNi}_{4.5}\text{Al}_{0.5}$ alloy by the self-reduction method. We determined the structure and electrochemical properties of the composite with X-ray diffraction, SEM-EDX (scanning electron microscopy-energy dispersive using X-ray) analysis, and electrochemical measurements. We also characterized the parent $\text{LaNi}_{4.5}\text{Al}_{0.5}$ alloy for comparison.

2. Experimental methods

The parent $\text{LaNi}_{4.5}\text{Al}_{0.5}$ alloy (provided by Xiamen Tungsten Co. Ltd., Xiamen, China) powder (<400 mesh) was dispersed in $\text{AuCl}_3\cdot\text{HCl}\cdot 4\text{H}_2\text{O}$ aqueous solution and then heated to 60°C under magnetic stirring for 4 h. The mixture was filtered and washed with deionized water and then dried at 80°C for 12 h under vacuum.

We examined the structure of the alloy by means of a Thermo X'TRA X-ray diffractometer with a $\text{Cu K}\alpha$ radiation source. We determined the surface morphology and elements distribution on the surface of the alloy particles by using a Hitachi S-4700 scanning electron microscope and a Thermo NORAN X-ray microanalysis system.

To prepare the testing electrode, we mixed the doped alloy powder (0.85 g) with carbon black (0.05 g), polytetrafluoroethylene (0.1 g) and suitable water and then smeared the mixture onto a $1.0\text{-cm} \times 1.0\text{-cm}$ foam nickel sheet (porosity >95%), to which we point-welded a nickel wire to serve as a current collector. After drying the mixture at 80°C under vacuum, we applied 10 MPa of pressure to the testing electrode.

We carried out the electrochemical experiments in a three-compartment electrode system consisting of a testing electrode, a counter electrode made of nickel foam, and an Hg/HgO electrode as the reference electrode. The electrolyte used as the fuel was 1 M KBH_4 in 2 M KOH aqueous solution (1 M KBH_4 –2 M KOH), and the electrolyte in the counter electrode compartment and the reference electrode compartment was 2 M KOH aqueous solution. All experiments were carried out at a temperature of 40°C . During the discharge process, the generated hydrogen was collected by a water replacement method to calculate the utilization efficiency of the fuel and evaluate the catalytic activity of alloys used as anodic materials in the borohydride fuel cell.

3. Results and discussion

3.1. Structure of the Au-doped alloy

The X-ray diffraction pattern of alloys is shown in Fig. 1. The body of alloys was consisted of $\text{LaNi}_{4.5}\text{Al}_{0.5}$ with a typical hexagonal CaCu_5 -type crystal structure. The doped Au could be seen, as shown in the figure.

Fig. 2 presents the scanning electron microscope images and elements distribution on the surface of particles doped with 2.0 wt% Au. Fig. 2(a) and (b) shows that the alloy powder was composed of homogeneous particles with sizes of approximately 20–30 μm . Fig. 2(c) shows the magnified surface image of the particles. Clearly, an alveolate structure formed on the surface of the alloy particles doped with Au, and the diameter of the hole was less than 100 nm. The structure was similar to the structure of AAO (porous aluminum anodic oxide) on the Al film [14]. The element distribution on the surface of the particle is shown in Fig. 2(d)–(h). Experimental results suggested that the elements, Au, La, Ni, Al, and O, were distributed evenly on the surface of the particle. The surface of the alloy particle was covered by fine Au particles, as shown in Fig. 2(d). Nickel still had the largest content on the surface of alloy parti-

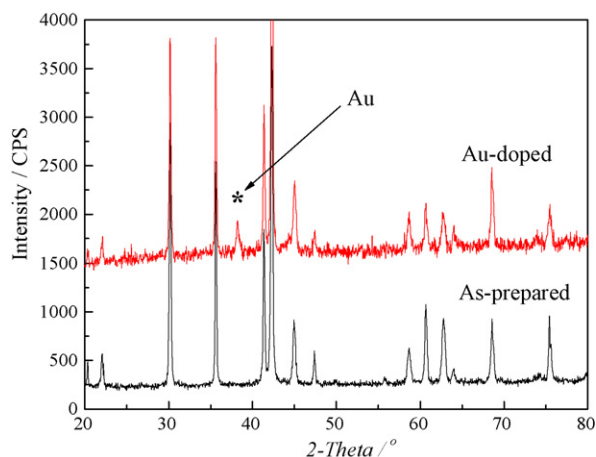


Fig. 1. X-ray diffraction pattern of the $\text{LaNi}_{4.5}\text{Al}_{0.5}$ alloy doped with 2 wt% Au.

cles, as shown in Fig. 2(f). We also observed considerable levels of oxygen, which could be attributed to the formation of lanthanum oxide and aluminum oxide during the self-reduction reaction with Au ion. The alveolate nano-structure on the surface of particles was attributed to the formation of these oxides.

Table 1 presents quantitative analysis of the elements on the surface of the $\text{LaNi}_{4.5}\text{Al}_{0.5}$ alloy doped with 2.0 wt% Au. The Au content on the surface of the alloy was only 0.89 wt%, less than the calculated 2.0 wt%. Part of Au may be embedded in the bulk of the alloy particles.

3.2. Discharge characteristic of the alloy electrodes

After immersing the electrodes in 1 M KBH_4 –2 M KOH solution (the fuel) for 4 h, we carried out the discharge experiments at various current densities. Fig. 3 shows the polarization curves and power density of alloy electrodes doped with Au. After modification with Au, the discharge potential and power density of the electrodes increased compared with that of the parent alloy. This finding suggested that the modification of Au enhanced the electrochemical catalytic activity of the electrode. The largest discharge current density increased from about 150 mA cm^{-2} (discharge to -0.6 V versus the Hg/HgO electrode) with the parent alloy to 250 mA cm^{-2} with the Au-doped alloy. The power density of the electrode made of the Au-doped alloy was approximately 150 mW cm^{-2} , much higher than that of the parent alloy electrode. The electrode made of Au-doped alloy was suitable for a high-rate discharge.

During the discharge process, the generated hydrogen was collected to calculate the fuel utilization by the following method [15]:

$$R_{\text{utilization}} (\%) = \frac{E_{\text{electricity}}}{E_{\text{electricity}} + E_{\text{hydrogen}}} \times 100. \quad (3)$$

where $E_{\text{electricity}}$ was the discharged electrical energy and E_{hydrogen} was the generated hydrogen energy.

Table 1
Surface quantitative analysis of the $\text{LaNi}_{4.5}\text{Al}_{0.5}$ alloy doped with 2 wt% Au

Element	wt%
O	2.6
Al	5.57
Ni	65.99
La	25.29
Au	0.89
Total	100

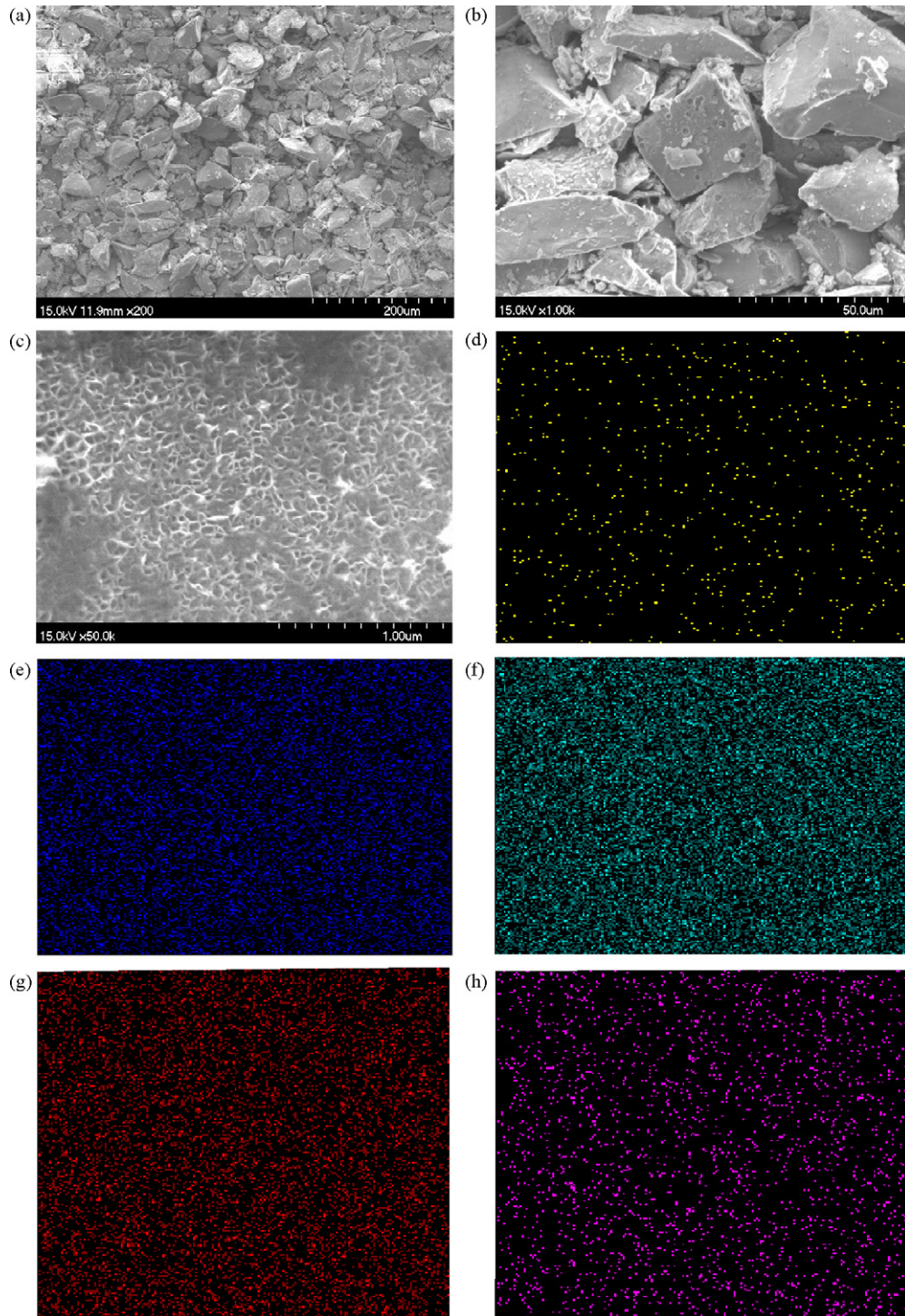


Fig. 2. Surface morphology and element distribution on the surface of $\text{LaNi}_{4.5}\text{Al}_{0.5}$ alloy doped with 2 wt% Au: (a–d) surface morphology, (e) Au, (f) La, (g) Ni, (h) Al and (i) O.

Fig. 4 presents the utilization of the fuel during the discharge process. The Au-doped alloys showed higher utilization of fuel than did the parent alloy. Experimental results revealed that the electrochemical oxidation during the discharge process was enhanced after Au modification. However, the modification had a larger effect on the electrochemical oxidation of the fuel than did the hydrolysis side reaction, which resulted in higher fuel utilization at large discharge current density. This finding suggested that Au modification was helpful to the high-rate discharge of the borohydride fuel cell. But the utilization efficiency of the fuel was not enhanced with the

increase of Au content because part of Au was embedded in the bulk of the alloy particles.

3.3. Electrochemical properties of the alloy electrodes

We determined the electrochemical properties of the alloy electrodes during the discharge process by using cyclic voltammetry. Fig. 5 shows the cyclic voltammetry curves of the electrodes at a scanning rate of 5 mV s^{-1} . Curves 1 and 2 were carried out in 2 M KOH solution, and curves 3 and 4 were carried out in 1 M

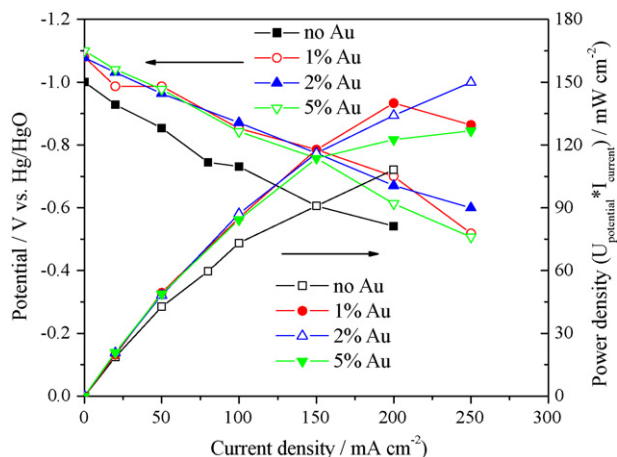


Fig. 3. Polarization curves and discharge power density ($U_{\text{potential}} \times I_{\text{current}}$) of alloy electrodes doped with Au in 1 M KBH_4 -2 M KOH solution.

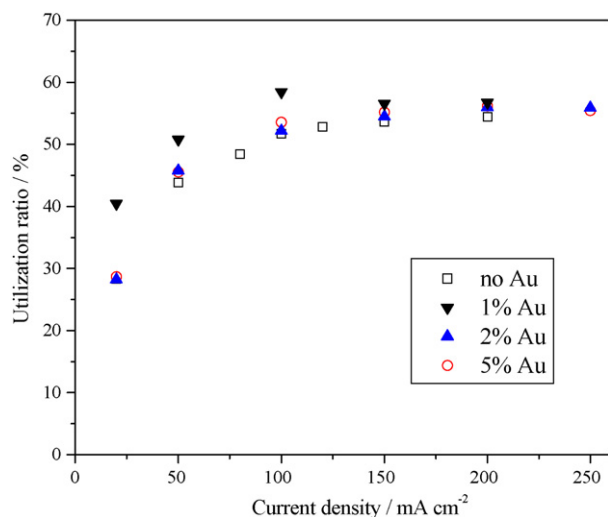


Fig. 4. Utilization of the KBH_4 -KOH fuel when using the Au-doped $\text{LaNi}_{4.5}\text{Al}_{0.5}$ alloy as the catalyst.

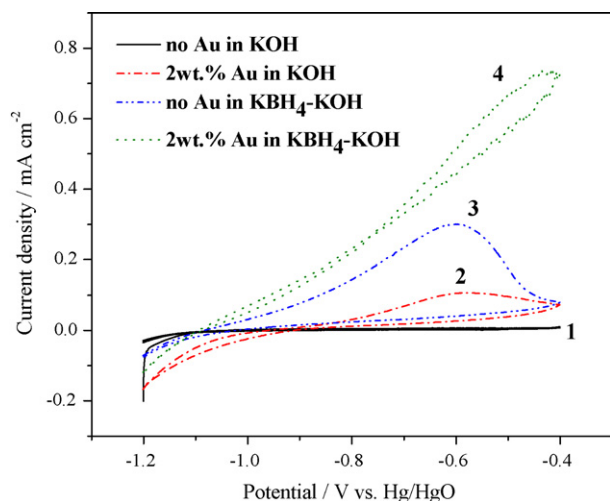
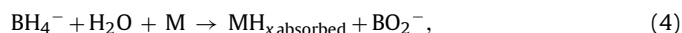


Fig. 5. Cyclic voltammogram curves of the electrode made of alloys at a scanning rate of 5.0 mV s^{-1} .

KBH_4 -2 M KOH solution. During all the scanning processes in BH_4^- content solution, we observed continuous hydrogen generation, which could be attributed to the side reaction, hydrolysis of borohydride. There was an anodic peak around -0.6 V versus Hg/HgO in curves 2 and 3, which could be ascribed to the oxidation of hydrogen absorbed on the surface of the polycrystalline electrode-based alloy [16]. This result indicated that part of the generated hydrogen was absorbed on the surface of the electrode and then transformed into electrical energy, as described by the following [17]:



The reaction current density of the electrode made of the Au-doped alloy was clearly much larger than that of the parent alloy. This finding suggested that the modification of Au on the surface of the alloy enhanced the electrocatalytic activity. Comparing curves 1 and 2 with curves 3 and 4, we found that the electrode in borohydride solution showed much larger current density, and the direct oxidation of borohydride that occurred was catalyzed by the hydrogen storage alloy. Unfortunately, evaluating how many electrons were directly converted during the discharge process was difficult because of the hydrolysis of BH_4^- that accompanied H_2 generation. Comparing curves 3 and 4, we found that the anodic peak around -0.6 V versus Hg/HgO disappeared in curve 4, but the current density was increased from 0.3 A cm^{-2} to 0.6 A cm^{-2} . This change may be attributed to the high electrocatalytic activity of the Au-doped alloy.

4. Conclusions

This report characterizes $\text{LaNi}_{4.5}\text{Al}_{0.5}$ alloy modified with Au used as the anodic catalyst in a direct borohydride fuel cell. Gold was evenly distributed on the surface of the alloy, and an alveolate structure was formed and the diameter of hole was less than 100 nm . After modification with Au, the electrocatalytic activity of the electrode was enhanced, and the largest discharge current density increased from about 150 mA cm^{-2} (discharge to -0.6 V versus the Hg/HgO electrode) with the parent alloy to 250 mA cm^{-2} with the Au-doped alloy. The power density of the electrode made of the Au-doped alloy was around 150 mW cm^{-2} , much higher than that of the parent alloy electrode.

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