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Electrochemistry Communications 7 (2005) 1477–1481
electrochemistry communications
www.elsevier.com/locate/elecom

Rare earth hydrogen storage alloy used in borohydride fuel cells

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Received 21 September 2005; received in revised form 11 October 2005; accepted 11 October 2005
Available online 9 November 2005

Abstract

Fuel cell using the borohydride as the fuel has attracted much attentions because of high energy density and working potential. In this work, $LaNi_{4.5}Al_{0.5}$ hydrogen storage alloy used as the anodic material to replace noble metals has been investigated. Experimental results showed that H_2 evolution was unavoidable during discharge process because of the hydrolysis of BH_4^-, but the utilization of the fuel increased with the increasing current densities. At high discharge current, the alloy electrode showed the lowest hydrogen generation rate and higher utilization of the fuel because, the generated hydrogen was absorbed and oxidized to produce electric energy similar to the behavior of hydrogen storage alloy in nickel–metal hydride batteries. The reaction mechanism of borohydride on the surface of electrode made of hydrogen storage alloy also has been discussed. Hydrogen storage alloy would be a promising material as the anodic catalyst in borohydride fuel cell.

Keywords: Borohydride fuel cell; Hydrogen storage alloy; Hydrogen evolution; Utilization of fuel

1. Introduction

Fuel cells are attractive alternative energy conversion devices due to their higher efficiency and low pollution. Borohydrides (MBH_4, M = Na, K, Li) present promising choices for electrochemical power sources either as hydrogen sources or fuels for direct borohydride fuel cells. The direct borohydride fuel is based on a complete eight-electron reaction process and provides a high theoretical specific capacity (5.7 A h g^{-1}, based on $NaBH_4$) and high cell voltage (1.64 V):

$$BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^-, \quad \phi^0 = -1.24\ V \tag{1}$$

Another advantage of borohydride fuel cell is that Ni-based catalysts can be used to replace the expensive noble metals [1]. Indig and Snyder [2] proposed direct borohydride fuel cells in the early 1960s using sintered Ni anode. The anode reaction was a four-electron reaction and the potential was around −1.125 V vs. HgO/Hg at a current density of 200 mA cm^{-2}.

Jasinski [3] compared the electrochemical performances of Pt, Pd and Ni_2B electrodes in KBH_4–KOH solution and found that Ni_2B showed good electrocatalytic activity for the oxidization of KBH_4. The utilization of the fuel was around 70% for the Ni_2B electrode due to the H_2 evolution and the reaction was described as a four-electron oxidation reaction of borohydride:

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

Amendola et al. [4] developed a borohydride fuel cell using Au–Pt alloy electroplated on carbon cloth as anode and a commercial gas diffusion electrode as cathode. The number of utilized electrons was around seven out of a total of eight electrons calculated on Eq. (1). Li et al. [5,6] and Lee et al. [7] reported Zr–Ni hydrogen storage alloys as the anode materials. A complete borohydride fuel cell has been developed and showed high power density [6]. Choudhury et al. [8] developed a fuel cell using sodium

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doi:10.1016/j.elecom.2005.10.012

borohydride as the fuel and hydrogen peroxide as oxidant, and various AB_5 and AB_2 alloys was used as the anode materials. A peak powder density of ca. 150 mW cm^{-2} at a cell voltage of 540 mV can be achieved from an optimized condition at 70 °C.

Gyenge [9] studied the electrochemical oxidation of BH_4^- on Pt and Au electrodes by various electrochemical methods and found that the addition of TU (thiourea) could improve the BH_4^- utilization efficiency and the coulombic efficiency of direct borohydride fuel cells because, the addition of TU minimized the catalytic hydrolysis of BH_4^- on Pt electrode.

In all these cases, H_2 evolution was unavoidable during the discharge process, which resulted in the low coulombic efficiency of BH_4^- oxidation calculated based on Eq. (1). In our previous works [10,11], the catalysts showed high electrochemical catalytic activity to the oxidation of BH_4^-, and also presented high catalytic hydrolysis to change BH_4^- into H_2.

In this work, we want to explore the possibility that AB_5-type hydrogen storage alloy is used as the anode materials in the borohydride fuel cell. Al element has been added to partly replace Ni in AB_5 alloy to lower the electrochemical activity, which would lower the catalytic hydrolysis of BH_4^-. At the same time, the slowly generated H_2 could be absorbed by the hydrogen storage alloy, and then converted to current, similar to those used in nickel–metal hydride batteries [12,13].

2. Experimental

The as-prepared $LaNi_{4.5}Al_{0.5}$ alloy was provided by Xiamen Tungsten Co. Ltd. The crystal structure of the alloy was examined by means of a Thermo X'TRA X-ray diffractometer with Cu Kα radiation source.

To prepare the testing electrode, the alloy powder samples (0.9 g) was mixed with carbon black (0.1 g) and 60 wt% polytetrafluoroethylene (PTFE) solution (0.1 g), then the mixture was smeared onto a 1×1 cm foam nickel sheet (porosity > 95%) to which a nickel wire was point-welded as current collector. After drying at room temperature, the testing electrode was pressed under a pressure of 10 MPa.

A three-apartment electrode measurement system was composed of the testing electrode, a nickel foam as the counter electrode and an Hg/HgO electrode as the reference electrode. The electrolyte used as the fuel was 5 wt% KBH_4 in 30 wt% KOH aqueous solution. The cyclic voltammery experiment was carried out using a Solartron 1287. The scanning rate was 10 mV s^{-1} and the scanning range was −1.2 to −0.4 V vs. Hg/HgO electrode.

The discharging experiment was carried out in a DC-5 Charge/Discharge Unit controlled by a computer. The discharge current densities were 10, 20 and 50 mA cm^{-2}, respectively. During the discharge process, the generated hydrogen was collected by a water replacement method to evaluate the catalytic activity of the samples used as the anodic materials in the borohydride fuel cell (BFC) and then the utilization of the fuel was calculated.

3. Results and discussion

Fig. 1 shows the XRD patterns of $LaNi_{4.5}Al_{0.5}$ alloy provided by Xiamen Tungsten Co. Ltd. This alloy presents a typical hexagonal $CaCu_5$-type crystal structure. The value of cell parameters a and c are 5.0383 and 4.0311 Å, respectively. Because of the addition of Al element, the volume of cell unit of sample becomes larger than that of the original $LaNi_5$ alloy. It is reported [12,14] that partial replacement resulted in larger cell unit volume and more defects was helpful to diffusion and storage of hydrogen in hydrogen storage alloy bulk. The addition of Al element, which results in expanded lattice, would be beneficial to absorb and store the hydrogen generated due to the hydrolysis of borohydride, and improve the utilization of the fuel.

Fig. 2 shows the discharge curves of the electrode in KBH_4–KOH solution. After immersion in KBH_4–KOH solution for 4 h, the solution has penetrated into the electrode and the OCP (open-circuit potential) of the electrode was around −0.98 V vs. Hg/HgO shown in curve A. The hydrogen bubbles produced continuously in this process, which could be attributed to the hydrolysis of borohydride described as Eq. (3). At the beginning of discharge, the potential of the electrode decreased quickly, and then gradually increased during the discharge process due to the activation of alloy electrode further:

$$BH_4^- + 2H_2O \rightarrow BO_2^- + 4H_2 \uparrow \quad (3)$$

Curves B, C and D show the discharge processes at current densities of 10, 20 and 50 mA cm^{-2}, respectively. The discharge plateaus decreased with the increasing current densities because of the effect of over-potential. In these discharge curves, there were some undulated curves could be observed, which was resulted from the adsorption and separation of hydrogen bubbles on the surface of the electrode, which resulted in the change of interface area between electrode and electrolyte, and current densities. In curve D, the discharge plateau decreases gradually due to the concentration polarization and the reduction of concentration of the fuel.

Fig. 3 shows the generation rate of H_2 during discharge process because of the hydrolysis of borohydride. The generation rate of H_2 at 20 mA cm^{-2} discharge current was quicker than that at 10 mA cm^{-2}, however, the generation of rate H_2 at 50 mA cm^{-2} was much lower than that at 10 and 20 mA cm^{-2}. It was very different with the previous work [10,11], where the generation rate of hydrogen increased with the increasing discharge current densities, and the utilization ratio of the fuel also increased because of much quicker enhancement of the electrochemical oxidation rate of the fuel on the anode than the rate of a competitive side reaction. In order to give a reasonable explanation, the electrochemical measurement has been