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Rare-earth-based AB_5-type hydrogen storage alloys as hydrogen electrode catalysts in alkaline fuel cells

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Abstract

Hydrogen oxidation by noble-metal-free, rare-earth-based, AB_5-type catalysts was investigated in a double-layer hydrogen anode where the catalyst layer and the gas-diffusion layer were rolled together. The catalytic activity and operational stability were examined in a half-cell with 30 wt% KOH at 55 °C. The electrode had good catalytic activity for hydrogen oxidation and long-term stability over 1600 h at a current density of 40–50 mA/cm^2.

Keywords: AB_5-type hydrogen storage alloy; Alkaline fuel cell; Catalyst for hydrogen oxidation

1. Introduction

In recent years, fuel cells as power generators for zero-emission electric vehicles have attracted much attention from both government and industry. Fuel cell R&D is to a substantial part focused on the polymer electrolyte fuel cell (PEFC) due to its high power density. However, the high cost of the cell components prevents its commercialization. Another problem is that the platinum catalyst is readily poisoned by carbon monoxide. It has been reported that even 10 ppm CO in the hydrogen feeding gas has a detrimental effect on fuel cell performance [1]. Thus, development of CO-tolerant catalysts is desired [2–4]. Increasing the operational temperature above 100 °C can reduce the absorption of CO onto the platinum catalyst. At higher temperatures, however, water readily vaporizes from the membrane and leads to drying out of the membrane. As a result, the ionic conductivity of the membrane is reduced and subsequently causes cell failure. To maintain an adequate membrane moisture level at elevated temperature, one or both of the feeding gases must be humidified. This increases both the complexity and the cost. Also, the mechanical strength of the membrane is lost by being softened at high operational temperatures, especially at temperatures above 120 °C. Thus, the operational temperature range is strictly limited by the features of the polymer membrane.

Alkaline fuel cells (AFCs) do not require an expensive polymer membrane and use a low-cost aqueous solution of potassium hydroxide as electrolyte. With the greater ionic conductivity of the electrolyte, AFCs have a higher available power capability. In addition, AFCs have other advantages over PEFC such as high efficiency (70–80%) and a wide range of operational temperatures. AFCs have been in use for more than 30 years by NASA's manned spacecraft. However, the cost of the system is still the major barrier if it is to be used in electric vehicles, since conventional AFCs use platinum catalysts in both electrodes. A very high platinum loading is also necessary for a high power rating. Therefore, it is essential to find a platinum-free catalyst.

Rare-earth-based, AB_5-type hydrogen storage alloys have the ability to absorb hydrogen at room temperature. They have been investigated extensively as negative electrodes in rechargeable Ni/metal hydride (NiMH) batteries. They have also been tested as hydrogen oxidation catalysts in AFCs [5,6]. In these initial tests, the performance rapidly degraded and the activity for the hydrogen oxidation reaction was low.

In the present study, we attempted to improve the performance of rare-earth-based, AB_5-type hydrogen stor-

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age alloy electrodes by designing a partially hydrophobic catalyst for good contact with the hydrogen gas and partial wetting of the catalyst for electrolyte transport, and to demonstrate that excellent stability in 30 wt% KOH solution at 55 °C can be achieved at a current density of 40–50 mA/cm^2.

2. Experiment

2.1. Catalyst and electrode preparation

An AB_5-type hydrogen storage alloy having an electrochemical capacity of 320–330 mAh/g was used as catalyst for a hydrogen oxidation electrode. Prior to electrode preparation, the hydrogen storage alloy was activated by three successive hydrogen absorption/desorption cycles. This process pulverizes the alloy powder into a particles size of 5–30 μm. The hydrogen oxidation electrode was prepared by a rolling method. First, a dough was made by blending MH alloy particles and carbon powder with a 10–30 wt% PTFE solution. The dough was then rolled to 0.4 mm thickness and then rolled together with a nickel net. Finally, the electrode was cold-pressed at 150–200 kg/cm^2 onto a gas-diffusion layer. The gas-diffusion layer consisted of highly wet-proof PTFE and black carbon. The final hydrogen oxidation electrode had a thickness of 0.6–0.8 mm and an area of 5 cm^2.

2.2. Measurement of electrode performance

The electrodes were tested in a half-cell. Steady-state current–potential curves of the electrode were measured in an aqueous solution of 30 wt% KOH at 55 °C without IR correction. The counter-electrode was a large nickel screen and the reference electrode was a Hg/HgO electrode with the same electrolyte solution. The electrode stability was also examined by applying a constant current density at 55 °C.

3. Results and discussion

3.1. Electrode features

The hydrogen oxidation electrode consisted of a gas-diffusion layer and a catalyst layer. The gas-diffusion layer supplies the reactant gas to the catalyst layer and should prevent any penetration of electrolyte. Therefore, porosity and hydrophobicity are critical parameters. To meet the requirements, this layer was composed of 64 wt% PTFE, 15 wt% back carbon and 21 wt% ammonium hydrogencarbonate.

Inside the catalyst layer, a three-phase reaction (gas, electrolyte and catalyst) takes place. Hydrogen gas first contacts the catalyst (hydrogen storage alloy) to form a hydride phase, then an electrochemical oxidation reaction occurs where electrons are released. Good performance necessitates partial wetting of the catalyst by the electrolyte and partial hydrophobicity for good contact of the hydrogen gas with the catalyst. In this work, a hydrophobic binder (PTFE) and carbon black were combined to provide a channel for passage of hydrogen gas to the catalyst while the pores of the electrode and the partly uncovered catalyst allow electrolyte transport.

3.2. Electrode activation

The electrode was activated by using a lower anodic current density (15–20 mA/cm^2) in the 30 wt% KOH solution at 55 °C for one or several days. In order to shorten the activation period, the electrode was also activated electrochemically by cathode polarization with a current density of 6–20 mA/cm^2 at 55 °C for one or several hours. During the alternative activation process, hydrogen gas was supplied from the backside of the electrode. Fig. 1 shows the activation behavior of the electrode at a low anodic current density. It is clear that the overpotential for hydrogen oxidation decreases in this phase. This indicates that wetting of the catalyst layer was improved and the polarization resistance of the electrochemical oxidation reaction was reduced with increasing reaction sites. Fig. 2 shows changes in the potential with operation time after the cathode activation process. The results show that the overpotential for hydrogen oxidation is further reduced and the electrode performance is improved. However, it is very important to control the activation time and the applied cathode current. If the catalyst layer is wetted too much, the electrode will lose long-term operational stability. Fig. 3 shows the dependence of the anode potential on the operation time after over-activation. The electrode could not maintain a steady operation potential and the performance deteriorated. The

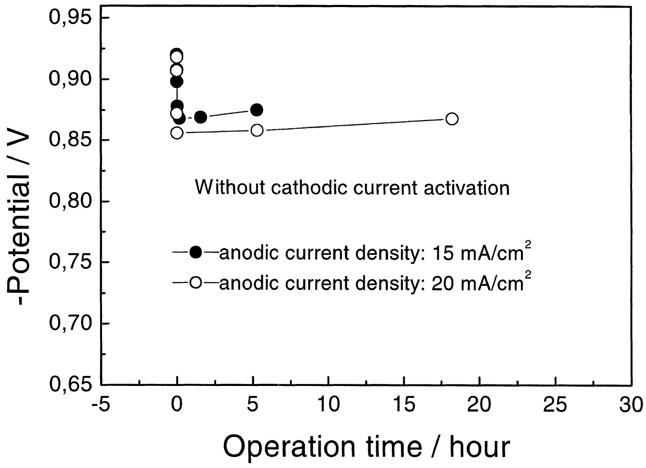

Fig. 1. Dependence of potential on activation time.

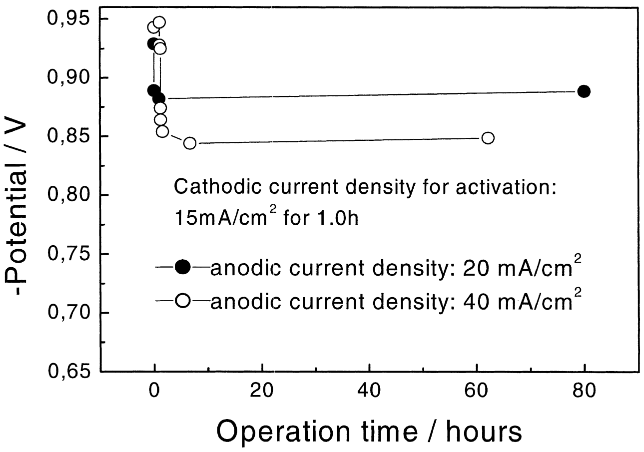

Fig. 2. Dependence of potential on time after cathode activation.

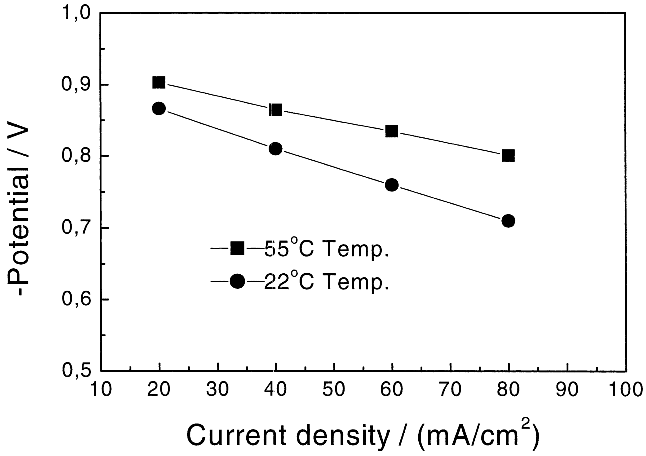

Fig. 4. Polarization curves of the electrode.

electrochemical behavior of the too wet electrode is similar to the metal hydride electrode used in NiMH cells. When hydrogen gas transport to the catalyst particles becomes difficult, the reaction rate decreases. Therefore, electrode activation has two main purposes. The first is to cause the electrolyte to penetrate into the catalyst layer and partly wet the catalyst particles. The second is to reduce oxidation of the catalyst, since the catalyst particles are readily oxidized during electrode fabrication in air. Another benefit is to increase the reactive area when the catalyst particles are broken up during electrochemical activation as the hydride is formed.

3.3. Electrode polarization and long-term test

The polarization curves for hydrogen oxidation at two temperatures are shown in Fig. 4. The polarization resistance is reduced with increasing operational temperature, since the electrode reaction rate and the hydrogen diffusion rate usually increase with increasing temperature. In addition, the PTFE content, hydrophilic material content, catalyst loading, catalyst particle size, electrode fabrication procedure, etc. also influence the polarization behavior. In this work, we did not optimize these parameters. Therefore, further optimization of the hydrogen oxidation electrode is necessary. The long-term stability was tested using two current loads, 40 and 50 mA/cm^2. Fig. 5 shows the variation of the potential versus the operation time. The electrode exhibited excellent performance and maintained good catalytic activity for hydrogen oxidation for 700 h at a current density of 40 mA/cm^2. Subsequently, a higher current load of 50 mA/cm^2 was applied to further examine its stability. As shown in Fig. 5, the electrode appears to have good long-term stability after another 900 h operation. The results are promising, as hydrogen storage alloys can replace the expensive Pt catalyst. However, it is necessary to further improve the electrode structure to attain a higher anodic current density, say 100 mA/cm^2, which is the target for our ongoing R&D.

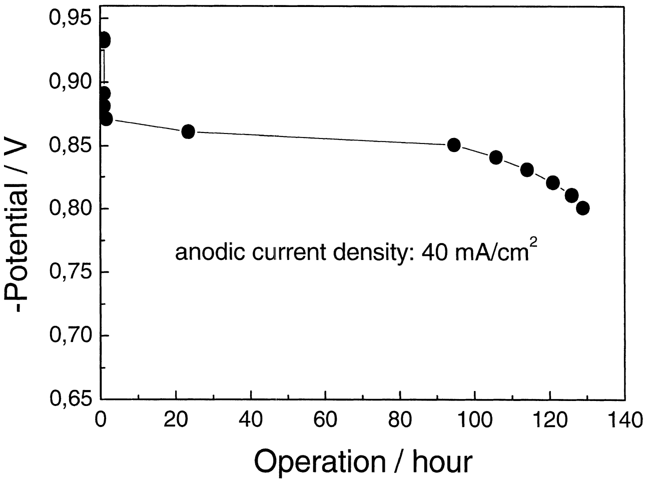

Fig. 3. Electrode performance after over-wetting.

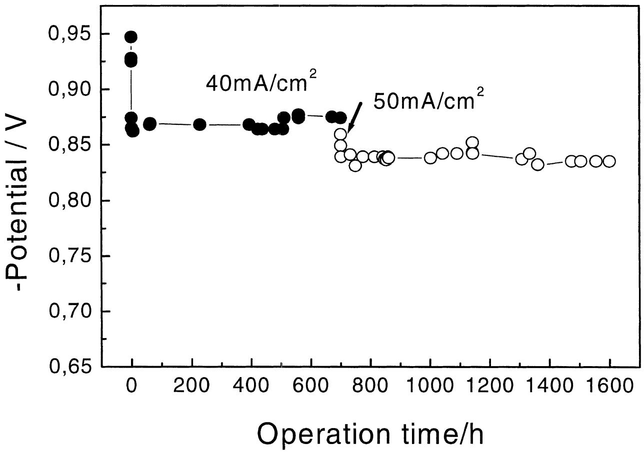

Fig. 5. Potential changes versus operation time.

4. Conclusion

A gas-diffusion electrode for hydrogen oxidation in AFCs was fabricated by a rolling method. The catalyst layer was composed of AB_5-type hydrogen storage alloy, carbon black and PTFE. The results show that the electrode has good catalytic activity for hydrogen oxidation and long-term electrochemical stability at a current load of 40–50 mA/cm^2 in 30 wt% KOH at 55 °C. Further improvement and optimization of the electrode composition and structure are necessary to obtain better performance at a higher anodic current density. The development of hydride alloys as noble-metal-free catalysts for hydrogen oxidation in future AFCs shows promise.

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