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Electrocatalytic abilities of hydrogen storage alloy as anode electrocatalyst of alkaline fuel cell

Y. Chen[a,b,c], C. Sequeira[b], T. Allen[c], C.P. Chen[a,*]

[a] Department of Materials Science & Engineering, Zhejiang University, Hangzhou 310027, China
[b] Department of Chemical Engineering, Instituto Superior Tecnico, Lisbon 1049-001, Portugal
[c] Department of Engineering Physics, University of Wisconsin-Madison, Madison, WI 53706, USA

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Abstract

The electrocatalytic abilities of hydrogen storage alloy (HSA) $MlNi_{3.65}Co_{0.85}Al_{0.3}Mn_{0.3}$ (Ml: La-rich mischmetal) as the anode electrocatalyst of an alkaline fuel cell were studied. To improve the electrocatalytic activity of the alloy, modifications including ball-milling, surface treatment and chemical coating with Pd were employed. The electrocatalytic ability of the optimized HSA anode was found to be reasonably good, with a current density of 50 mA/cm^2 at 0.866 V and 196.2 mA/cm^2 at 0.5 V (versus Hg/HgO). The temperature was also found to be important for the electrocatalytic behavior of HSA anode.

Keywords: Hydrogen storage alloy; Alkaline fuel cell; Anode; Electrocatalytic ability; Surface modification

1. Introduction

The application of low temperature type (<100 °C) alkaline fuel cells (AFC) as a primary power source in electric vehicles and portable equipment has received increasing attention. In an AFC system, platinum is usually chosen as an electrode electrocatalyst. However, Pt is limited for commercial use because of high cost and limited availability. Rare earth based AB_5 type hydrogen storage alloys (HSAs) used as electrode materials for nickel/metal hydride batteries are characterized by their good electrochemical properties, mechanical and chemical stabilities in alkaline electrolyte. Since the 1970s and 1980s, research groups have investigated using HSAs as the anode catalyst for AFC [1,2]. Previous work [3,4] indicated that using the AB_5-type HSA as an electrocatalyst for an AFC anode showed a catalytic effect [4]. However, this former research work also indicated that the electrocatalytic activities and the degradation rate of such anodes needed to be further improved to be sufficient for practical use.

In this work, the possibility of using typical HSA $MlNi_{3.65}Co_{0.85}Al_{0.3}Mn_{0.3}$ as the anode catalyst of AFC was investigated. To improve the electrocatalytic activity of the alloy, a series of modifications including ball-milling, surface treatment and chemical coating Pd were employed. The optimum structure and composition of the HSA anode were also studied.

2. Experiments

The as-cast $MlNi_{3.65}Co_{0.85}Al_{0.3}Mn_{0.3}$ alloy for the experiment was mechanically crushed into powders as sample 1 with a dimension of less than 200 mesh. Three different surface modification methods, including ball-milling (sample 2), ball-milling and surface treatment by hot alkaline solution containing reductant (sample 3), and ball-milling, surface treatment and chemically coated with Pd (sample 4), were employed. The sample was ball-milled for 0.5 h at a rate of 225 rpm under argon atmosphere. The surface treatment was carried out by immersing the sample alloy in a 6 M KOH solution containing 0.01 M KBH_4 at 80 °C for 3 h. A chem-

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[*] Corresponding author. Tel.: +86 571 8795 1152; fax: +86 571 8795 1152.
E-mail address: cpchen@zjuem.zju.edu.cn (C.P. Chen).

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ical coating solution, composed of $PdCl_2$, HCl, NH_4Cl and ammonia, was used for coating Pd and the coating amount was 2 wt.% Pd of the alloy.

The electrochemical measurements were performed in a typical electrochemical cell consisting of a working electrode, a sintered $Ni(OH)_2$ counter electrode, and a Hg/HgO reference electrode. The HSA electrodes for voltammetric measurement were performed at sweep rates of 10, 20, 40, 60, 80 and 100 mV/s at 25 °C. The EIS measurements for the MEA samples were performed with a frequency response analyzer (1255B) combined with Solartron SI1287 and an electrochemical interface driven by Zplot software. The impedance data generally covered the frequency range of 10 kHz to 5.0 mHz with 5 mV amplitude of the sinusoidal voltage and the Zview 2.0 software was employed for simulation and calculation.

The test HSA anode was designed and prepared with four layers, i.e. Ag-coated nickel net layer, electrocatalyst layer, diffusion layer and foam-nickel-sheet collector. The loading amount of the catalyst alloy was 0.5 g/cm^2. The reactant hydrogen pressure was 2 atm. Electrocatalytic tests of the HSA anode were performed in a three-electrode system consisting of a working anode electrode, a Pt counter electrode and a Hg/HgO reference electrode. The electrolyte was a 6 M KOH solution.

3. Results and discussion

3.1. *Effect of modifications on the electrochemical properties of hydrogen storage alloy*

Cyclic voltammograms of the as-cast $MlNi_{3.65}Co_{0.85}Al_{0.3}Mn_{0.3}$ alloy and the alloys with different modifications are shown in Fig. 1(a–d), respectively. As exhibited in Fig. 1, a hydrogen oxidation peak can be observed on the anodic branch of the cyclic voltammograms of each test electrode. With the increase of sweep rates, peak current densities are increased and their corresponding peak potentials are also apparently shifted to the positive direction. The values of peak currents and their corresponding potentials at 40 mV/s are listed in Table 1. It can be seen that after different modifications, the hydrogen oxidation peak current is increased at different degrees compared to that of as-cast alloys. After ball-milling, the peak current density of the alloy is 1.654 A/g, higher than that of the as-cast alloy (1.458 A/g). The increase of the peak current density is probably due to the enlargement of the specific surface area of the alloy as a result of the reduction of the particle and grain sizes after ball-milling. Ball-milling and surface treatment by a hot alkaline solution containing reductant caused the anodic oxidation peak current of the alloy to reach 1.725 A/g, after the addition of chemical coating with 2 wt.% Pd, caused a further increase to 2.088 A/g. After the alloy was treated by a hot alkaline solution containing reductant and was chemically coated with Pd, the surface of the HSA formed a Ni-rich layer and a Pd layer. In the meantime, the preferential dissolution of the elements such as Al and Mn during the treatment process enlarged the specific surface area of the alloy.

EIS spectra with discharge of depth DOD = 50% for four alloy samples were studied and their corresponding charge transfer resistances R_p, which are related to the semicircle in the low-frequency region, were evaluated by the Zview 2.0 software. The results are summarized in Table 2. Table

Table 1
Oxidation peak currents i_P and the corresponding oxidation peak potentials of the as-cast alloy and the alloys with different modifications at a sweep rate of 40 mV/s

	Sample 1	Sample 2	Sample 3	Sample 4
Oxidation peak current (A/g)	1.458	1.654	1.725	2.088
Oxidation peak potential (V) (vs. Hg/HgO)	−0.6475	−0.6453	−0.6389	−0.6369

Table 2
Charge transfer resistance R_p of the alloy samples at 25 °C and 50% DOD calculated by EIS

HSA electrode	R_p (Ω g)
Sample 1	1.157
Sample 2	1.064
Sample 3	0.7207
Sample 4	0.4244

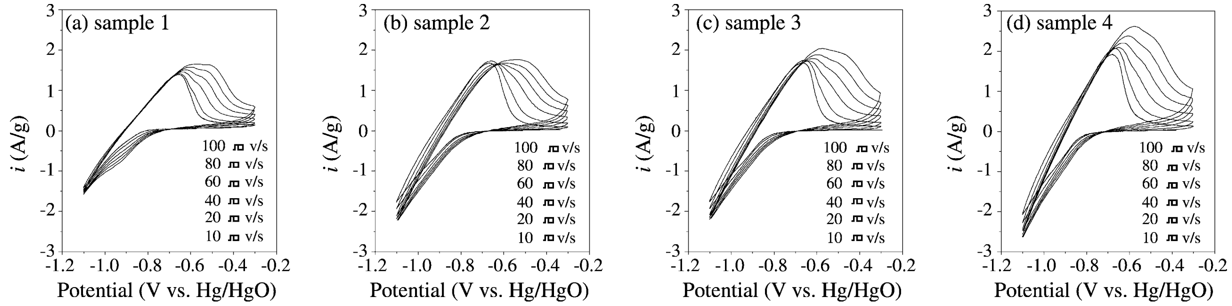

Fig. 1. Cyclic voltammograms of the as-cast alloy and the alloys with different modifications.

2 shows that the charge transfer resistances R_p is gradually decreased after ball-milling modification and the following surface modifications.

3.2. Electrocatalytic properties of the hydrogen storage alloy anode in AFC

To obtain the optimum structure and composition of HSA anode, several additional materials and concentrations in the anode electrocatalytic layer were investigated. The results indicate that the PTFE and the acetylene affect the anodic overpotential remarkably. The lowest overpotential of HSA anode without acetylene black in the catalyst layer can reach 0.1411 V with the corresponding PTFE amount ranging from 10 to 12 wt.%. After the addition of acetylene black, the lowest overpotential value of the HSA electrode is 0.0687 V, with the corresponding content of PTFE in the range of 14–22 wt.%. The experimental results show that the addition of acetylene black in the catalyst layer not only decreases the anodic overpotential but also improves the mechanical properties of the HSA anode.

To solve the problems of poor electric conductivity and the decrease of active material utilization caused from PTFE, we added a porous-form material, ammonium oxalate $(NH_4)_2C_2O_4$, into the HSA anode catalyst layer for increasing its porosity. The results show that 5 wt.% of $(NH_4)_2C_2O_4$ content is related to the lowest anodic overpotential and the best performance of anode electrode.

Based on the optimum structure and composition of the catalyst layers that containing 2 wt.% of acetylene black, 14–22 wt.% of PTFE and 5 wt.% of $(NH_4)_2C_2O_4$, respectively, four anodes were prepared using the HSA $MlNi_{3.65}Co_{0.85}Al_{0.3}Mn_{0.3}$ with different modifications as anode catalysts and the results are exhibited in Fig. 2. The discharge current could be observed only at very high anodic overpotential and the anode potential is only 0.392 V at 50 mA/cm^2 at 25 °C, indicating that the anode using the as-cast alloy shows rather bad electrochemical properties. After 30 min of ball-milling, the performance of the anode alloy is improved, with anodic potential increasing to 0.533 V. The remarkable improvement of the electrocatalytic properties could be observed when the anode alloy was ball-milled and then treated by alkaline solution containing KBH_4. And further improvement could be obtained when the foregoing modified alloy was chemically coated with 2 wt.% Pd which the anode potential was 0.866 V at a current density of 50 mA/cm^2.

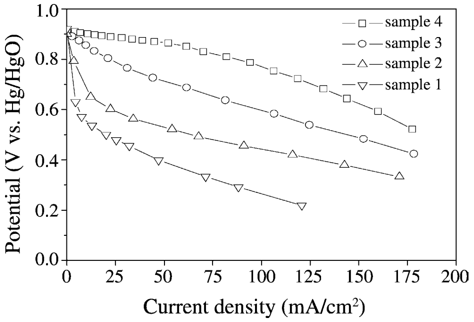

Fig. 2. Performance of the anodes using HSA with different modifications at 50 mA/cm^2 and 25 °C.

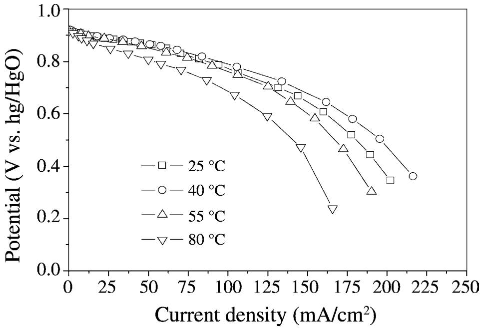

Fig. 3. Dependence of the performance of HSA anode on the different operating temperatures.

The electrocatalytic properties of the sample anodes at different temperatures of 25, 40, 55 and 80 °C were studied and the results are shown in Fig. 3. The electrocatalytic behavior of the optimized HSA anode was found to be relatively good. The HSA anode shows the best electrocatalytic properties, especially the property of large current density, when the operating temperature was 40 °C. A maximum current density of 196.2 mA/cm^2 at 0.5 V can be achieved at 40 °C. The overall performance of the HSA anode is not obviously influenced by the operating temperature in the range of 25–55 °C. However, when the operating temperature continuously increased to 80 °C, the electrocatalytic abilities of HSA anode decreased remarkably. One possible explanation is that metal hydride is the main electrocatalytic phase for HSA anode and the existence of hydride phase is strongly dependent on the hydrogen pressure and temperature. When the operating temperature increased to 80 °C at hydrogen pressure of 2 atm, hydrogen that was released from hydride made the remarkable decrease of electrocatalytic abilities of anode active material.

4. Conclusions

A series of modifications are obviously effective in the improvement of the electrocatalytic properties of a hydrogen storage alloy. The oxidation peak current densities are increased from 1.458 A/g of the as-cast alloy to 2.008 A/g when modified with ball-milling, surface treatment and chemical coating Pd; on the contrary, the charge transfer resistance is decreased from 1.157 to 0.4244 Ω g.

The electrocatalytic ability of the optimized AFC HSA anode is found to be reasonably good, with a current density of 196.2 mA/cm^2 at 0.5 V (versus Hg/HgO). The best electrocatalytic properties, especially the large current density properties, are achieved when the working temperature is 40 °C.

Acknowledgements

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