Journal of Alloys and Compounds 293–295 (1999) 833–837

Electrochemical properties of Ml(NiCoMnCu)$_5$ used as an alkaline fuel cell anode

X.H. Wang*, Y. Chen, H.G. Pan, R.G. Xu, S.Q. Li, L.X. Chen, C.P. Chen, Q.D. Wang

Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, PR China

Abstract

The electrochemical properties of AB$_5$-type rare earth–nickel multicomponent compounds Ml(NiCoMnCu)$_5$ (Ml: La-rich mischmetal) used as an alkaline fuel cell anode were investigated at 30°C. A double-layer porous film structure with foamed nickel as current collector was adopted for the anode. A catalyst layer made of Ml(NiCoMnCu)$_5$ alloy powder and a 60% aqueous suspension of polytetrafluoroethylene (PTFE) was on the electrolyte side, and a waterproof layer made of a Teflon aqueous suspension and Na$_2$SO$_4$ powder was on the gas side. The experimental results revealed that the anode performance strongly depends on the PTFE content of the catalyst layer, the thickness of the catalyst layer and the waterproof layer, and the cold compression pressure for electrode formation. When these four parameters were 12 wt.%, 0.25 mm, 0.2 mm and 12 MPa, respectively, the anode had a life-time of approximatly 550 h at a current density of 20 mA/cm^2. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Alkaline fuel cell; AB$_5$-type hydrogen storage alloy; Electrochemical properties

1. Introduction

Since the discovery of the AB$_5$ (LaNi$_5$) and AB (TiFe) families of hydrogen storage intermetallics and their hydrides in the 1970s by the pioneering work at Philips Laboratory in the Netherlands and at Brookhaven National Laboratory in the US, hydrogen storage alloys have been used extensively in many applications, namely in the processing of hydrogen in thermal storage, heat pumping and electrochemical charging/discharging [1–4]. In recent years, much attention has been paid to the electrochemical applications. Extensive work has been centered around nickel–metal hydride batteries using metal hydrogen storage intermetallic compounds as negative electrodes. This kind of rechargeable battery is in fact a reversible combination of a fuel cell and an electrolyzer. It is suggested that hydrogen storage intermetallic compounds can also be used as electrocatalysts for fuel cells [5,6].

One of the advantages of the alkaline fuel cell is the use of non-noble metal electrocatalysts [7]. Raney nickel [8] is a typical example of a non-noble metal electrocatalyst used for alkaline fuel cells. Our previous work has indicated that Ml(NiCoMnCu)$_5$ is a good negative electrode material for Ni–MH batteries. In the present work, we investigated the electrochemical properties of the hydrogen storage intermetallic compound Ml(NiCoMnCu)$_5$ as an alkaline fuel cell anode.

The anode was made to be a dual-layer structure with foamed nickel as current collector. The catalyst layer, made of Ml(NiCoMnCu)$_5$ alloy powder and a 60% aqueous suspension of PTFE (polytetrafluoroethylene), was on the electrolyte side, and a waterproof layer made of a PTFE aqueous suspension and Na$_2$SO$_4$ powder was on the gas side. The effects of the following factors on the electrochemical properties of the anode were studied: (1) PTFE content of the catalyst layer; (2) thickness of the catalyst thin film; (3) thickness of the waterproof thin film; (4) cold compression pressure for electrode formation.

2. Experimental details

The main contents of the La-rich mischmetal Ml used in the test were: La, 73.95%; Ce, 5.4%; Pr, 17.21%; Nd, 3.87%; Fe, 0.195%; Mg, 0.066%. The purity of metallic Ni, Co, Mn and Cu was >99%. The purity of the hydrogen used in the tests was 99.999%. The samples were prepared by arc-melting in a water-cooled copper crucible under argon atmosphere, and were remelted more than twice to assure good homogeneity. Samples were pulverized into powder with particle size <300 mesh by one of the

---

*Corresponding author.

PII: S0925-8388(99)00367-9

following two methods: (1) mechanical crushing and grinding; (2) hydrogen decrepitation.

The anode contained a catalyst thin film and a waterproof thin film with foamed nickel as current collector. The catalyst layer was prepared by first mixing hydrogen storage alloy powder, Teflon aqueous suspension and absolute alcohol, then heating in a hot water bath. Teflon was used as the binding material and also to adjust the hydrophobicity of the catalyst layer. Alcohol served as the deemulsification reagent. The waterproof thin film was prepared from a Teflon aqueous suspension and Na_2SO_4 powder with alcohol as deemulsification reagent. Na_2SO_4 powder with particle size <300 mesh served as pore-forming material. A flowchart for anode preparation is shown in Fig. 1. A schematic diagram of the anode structure is shown is Fig. 2.

Electrochemical tests were performed with a three-electrode system. The electrolyte was 6 M KOH and the temperature was controlled at 30°C. The electrode effective surface area was 1 cm^2. Continuously flowing fresh hydrogen was fed directly to the anode from behind with the reminant hydrogen vented to the atmosphere through a small tube. A nickel sheet was used as the counter electrode and a Hg/HgO electrode as the reference electrode.

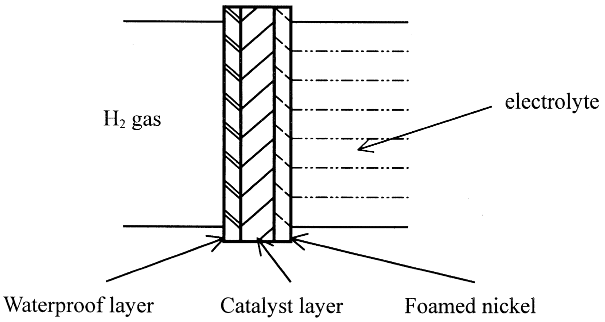

Fig. 2. Schematic diagram of the anode structure.

3. Results and discussion

3.1. Relationship between electrode performance and PTFE content of catalyst layer

On one hand, PTFE in the catalyst layer serves as a binding material which makes the catalyst powder easy to roll into a thin film. On the other hand, PTFE is a hydrophobic material which provides paths for hydrogen gas diffusion in the catalyst layer. Therefore, the content of PTFE in the catalyst layer plays an important role. To

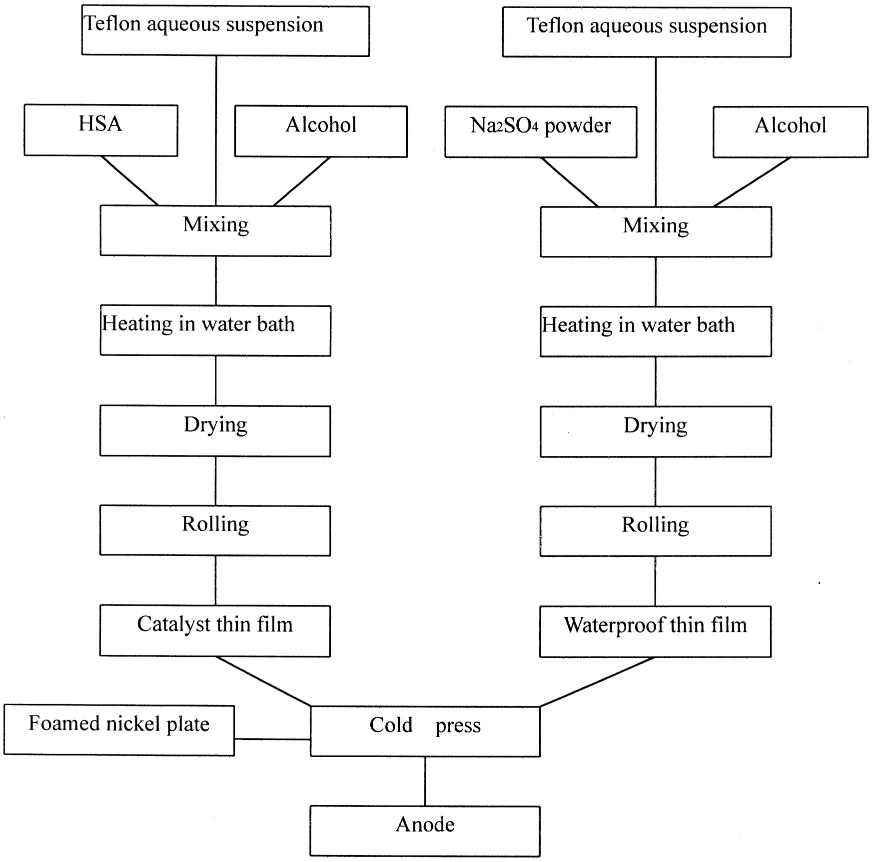

Fig. 1. Flowsheet for anode preparation.

some degree it determines the formation of the three-phase interface.

When the content of PTFE in the catalyst layer is too high, the electrochemical performance of the electrode deteriorates. Firstly, the higher the PTFE content, the lower the catalyst content. Secondly, PTFE is a non-conductive material, and a high PTFE content increases the ohmic resistance of the catalyst layer. Thus, ohmic polarization of the electrode increases. Finally, because PTFE is a hydrophobic material, a high PTFE content results in a good hydrophobicity but poor hydrophilicity of the catalyst layer. In this case, the three-phase interface cannot be formed readily.

On the contrary, when the PTFE content is too low, the rolling operation becomes difficult, and the catalyst thin film becomes brittle and breaks up easily. Furthermore, a low PTFE content leads to high hydrophilicity, which also makes the formation of the three-phase interface difficult. So, also in this case, the electrode has poor performance.

Therefore, there is an optimum PTFE content of the catalyst layer. We investigated the performance of electrodes with PTFE contents ranging from 5 to 15 wt.%. The thickness of the catalyst layer thin film and the waterproof thin film was 0.25 and 0.2 mm, respectively. The cold compression pressure for electrode formation was 10 MPa. Fig. 3 shows the relationship between the overpotential and the PTFE content at a current density of 50 mA/cm^2. When the PTFE content is in the range 10–12.5 wt.%, the electrode has the lowest overpotential.

3.2. Dependence of electrode performance on the thickness of the catalyst thin film

Fig. 4 shows the variation of the polarization curves of electrodes with different thickness of the catalyst thin film. It can be seen that when the thickness of the catalyst layer is 0.25 mm, the electrode has the best performance. As the thickness increases or decreases, the electrode performance becomes poorer. When the thickness of the catalyst layer increases, the transition distance for electrons, electrolyte and hydrogen gas all increase. This leads to a larger ohmic polarization and concentration polarization. When the thickness becomes smaller, the ohmic polarization and concentration polarization become smaller, however it is easy for hydrogen gas to pass through the electrode into the liquid chamber. In this case it is also difficult to form a three-phase interface, and the electrochemical reaction cannot proceed easily. Moreover, the ratio of cavities in the solid phase increases, resulting in a higher ohmic resistance of the solid phase.

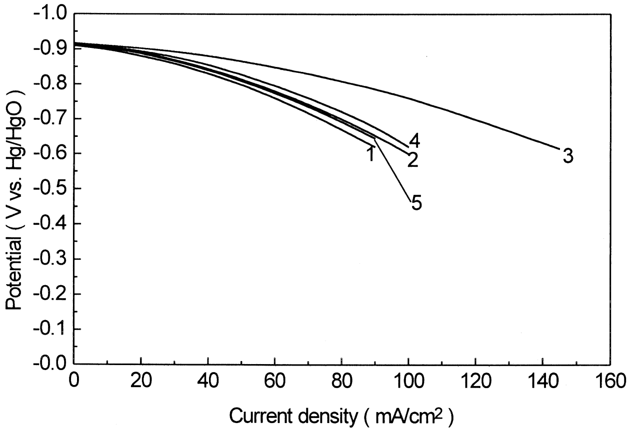

Fig. 4. Dependence of electrode performance on the thickness of the catalyst thin film: (1) 0.15 mm; (2) 0.2 mm; (3) 0.25 mm; (4) 0.3 mm; (5) 0.35 mm.

3.3. Dependence of anode performance on the thickness of the waterproof thin film

Fig. 5 shows polarization curves of anodes with different thicknesses of the waterproof layer. The test results indicate that there is an optimum thickness for the water-

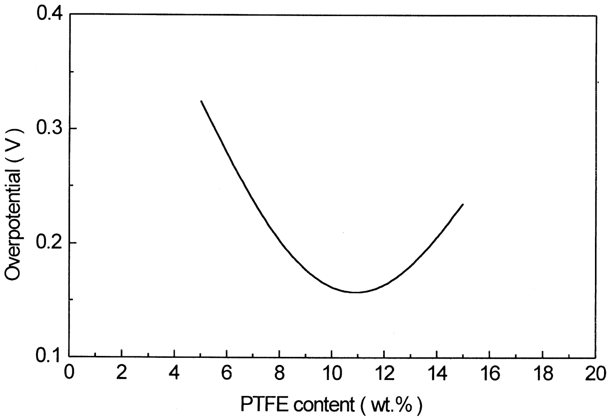

Fig. 3. Relationship between electrode performance and PTFE content of the catalyst layer.

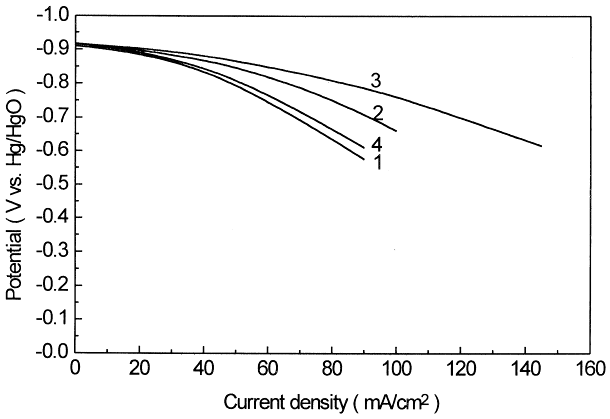

Fig. 5. Dependence of electrode performance on the thickness of the waterproof thin film: (1) 0.1 mm; (2) 0.15 mm; (3) 0.2 mm; (4) 0.25 mm.

proof layer. As this film becomes thicker, the gas diffusion distance increases. Thus the hydrogen concentration in the reaction interface decreases, resulting in a poorer electrode performance. On the other hand, when this film is too thin, its waterproof ability becomes poorer. Once the electrolyte permeates into the gas chamber, the electrode performance will deteriorate quickly.

3.4. Dependence of electrode performance on the cold compression pressure for electrode formation

With the thickness of the catalyst layer and the waterproof layer at 0.25 and 0.2 mm, respectively, we investigated the polarization curves of electrodes formed with different cold compression pressures ranging from 6 to 15 MPa. The optimum electrode formation pressure is about 12 MPa, as shown in Fig. 6.

As the pressure increases, both the porosity of the electrode and the average diameter of the pores decrease. Thus hydrogen transfer in the electrode becomes difficult, so the electrode performance becomes worse. On the other hand, when the pressure of electrode formation is too low, the catalyst thin film does not adhere firmly to the current collector, and the ohmic polarization increases.

3.5. Dependence of the anode potential on the time at different current loads

It is very important that the anode has a long life-time. Therefore, the anode potential versus time behavior at different current loads was investigated. Fig. 7 shows the dependence of the anode potential on time with current densities of 20, 50 and 80 mA/cm^2. The results indicate that when the current density was 80 mA/cm^2, the anode deteriorated rapidly and after 15 h the electrode was destroyed. When the current density was reduced to 50 mA/cm^2, the electrode survived for about 3 days. Further reduction of the current density to 20 mA/cm^2 leaded to life performance. The deterioration rate was 0.6 mV/h. When the cut potential was set to 0.6 V (vs. Hg/HgO), the predicted life-time was 550 h. However, the properties of the hydrogen storage alloy based anode were not comparable with those of the Raney nickel based electrode. It was reported that [8] a Raney nickel based electrode was destroyed after 200 h at a current density of 300 mA/cm^2, and a life-time of 5000 h was predicted at a current density of 100 mA/cm^2.

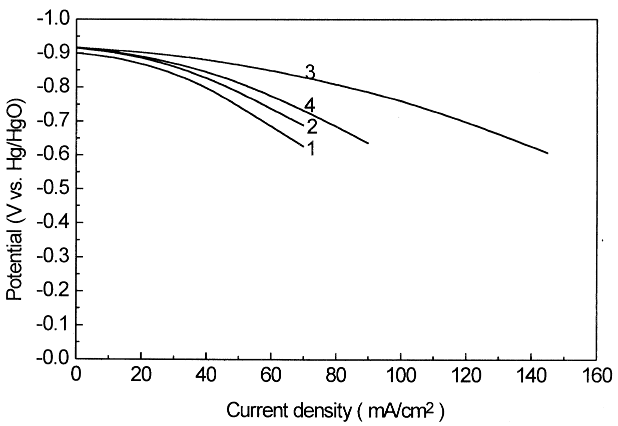

Fig. 6. Dependence of electrode performance on the cold compression pressure for electrode formation: (1) 6 MPa; (2) 9 MPa; (3) 12 MPa; (4) 15 MPa.

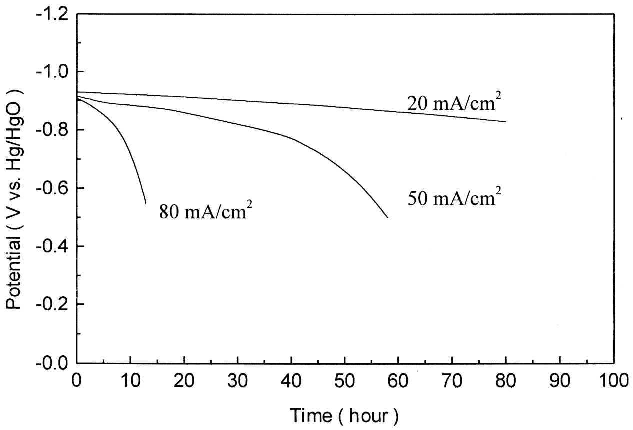

Fig. 7. Dependence of anode potential on the time at different current loads.

For the hydrogen storage alloy based electrode, when the overpotential was below 0.3 V, the deteriorated electrode could easily be reactivated by heating the electrode at 80–100°C under vacuum conditions. It is suggested that the hydrogen storage alloy catalyst did not deteriorate. It was also found that when the electrode deteriorated, the gas side of the electrode was wetted by the electrolyte. Thus the undesirable electrode performance was due to the bad waterproof properties of the electrode. Further improvement of the anode preparation technique is necessary.

4. Conclusions

1. The hydrogen storage intermetallic compound Ml(NiCoMnCu)$_5$ as an electrocatalyst of an alkaline fuel cell anode has a catalytic effect, but its properties should be further improved.
2. The electrode performance strongly depends on the PTFE content of the catalyst layer, the thickness of the catalyst layer and the waterproof layer, and the cold compression pressure for electrode formation. When these four parameters are 12 wt.%, 0.25 mm, 0.2 mm and 12 MPa, respectively, the anode has the best performance under our experimental conditions. The current density of the anode reached 145 mA/cm^2 at an overpotential of 0.3 V. The predicted life-time of the electrode was approximatly 550 h at a current density of 20 mA/cm^2.

References

[1] J.H.N. van Vucht, F.A. Kuijpers, H.C.A.M. Bruning, Philips Res. Rep. 25 (1970) 133.

[2] J.J. Reilly, R.H. Wiswall, Inorg. Chem. 13 (1974) 218.

[3] L. Schlabach, Hydrogen in Intermetallic Compounds, Vol. I, Springer, Berlin, 1988.

[4] L. Schlabach, Hydrogen in Intermetallic Compounds, Vol. II, Springer, Berlin, 1988.

[5] N. Kaneki, H. Hara, K. Tokuhashi, Y. Jomoto, J. Chem. Soc. Jpn. 14 (1981) 613.

[6] K. Viden, in: A.F. Andresen, A.J. Maeland (Eds.), Proceedings of an International Symposium, Geilo, Norway, 1977, Hydrides for Energy Storage, Vol. 463, Pergamon Press, Oxford, 1978.

[7] K. Koordesch, G. Simader, Fuel Cells and Their Applications, Vol. 54, VHC Verlagsgesellshaft mbH, Veinheim, 1996.

[8] W. Jewnseit, A. Khalil, H. Wendt, J. Appl. Electrochem. 20 (1990) 893.