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Metal hydride electrodes with lamellar-type network structure

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Abstract

New types of metal hydride electrodes with three dimensional networks of conducting metal powder have been developed. Utilization efficiency of the alloy was successfully improved because of elimination of the usual non-conductive polymeric binder and also the material cost could be reduced because it was not necessary to use an expensively formed nickel substrate or an expensive surface coating process. The new electrodes are composed of hydrogen storage alloy and newly developed flake-type copper and/or nickel powder formed into a laminated network structure in the electrode, thus providing better binding ability and better electrode conductivity than a conventional dendritic powder. The mixture, in the weight ratio of Cu(Ni)/alloy=0.2, was press-bound on a nickel mesh current collector. The effect of flake powder was more pronounced for the Ti–Zr based AB_2 type alloy (less conductive surface) than the rare earth based AB_5 type alloy.

Keywords: Flake copper powder; Flake nickel powder; Conducting materials; Hydrogen storage alloy; Nickel–metal hydride battery

1. Introduction

Recently, the demand for nickel–metal hydride (Ni–MH) batteries has been growing rapidly for use in small cordless appliances such as mobile telephones and laptop computers and also in electric vehicles. Research efforts are focused toward achieving higher energy densities (volume and weight), higher power capability, longer cycle life and lower cost [1]. Most of the processes to prepare the electrodes are based on a wet technique in which a mixture of alloy powder for a negative electrode (or nickel hydroxides for a positive one) is made with polymeric binders, and pasted or packed into porous nickel substrates.

A dry powder process has been proposed recently [2] in which the mixture of active materials and carbonyl nickel powder was press-bound on the nickel mesh to prepare the electrodes without polymeric binders, expensive formed nickel and discharge of waste water. The electrodes, made by the dry process, showed nearly comparable performances with the previous ones in a sealed cell, but further improvement of binding ability was needed.

The authors have developed flake-type copper and nickel powders which can be used to form a lamellar-type network structure in the electrodes [3]. The MH electrodes showed higher capacity and also higher mechanical strength because the flake powder could effectively microencapsulate the alloy surface, and it could also form a three dimensional network structure. In this paper, the effect of the flake metal powder versus the conventional dendritic powder on improving electrode performances will be reported.

2. Experimental details

Hydrogen storage alloys of composition $MmNi_{3.5}Co_{0.7}Al_{0.8}$ (Mm=mischmetal, AB_5 type alloy) and $Ti_{0.5}Zr_{0.5}Ni_{1.3}V_{0.7}Mn_{0.1}Cr_{0.1}$ (AB_2 type alloy) with an average grain size of 75 μm were used. Newly developed flake copper and nickel powders (Fig. 1) were used as both binding and conducting materials for preparing the electrodes. The mean particle size and specific surface of the powders were −10 μm and −20 000 cm^2 g^{-1}, respectively, which were much smaller and higher compared to those of the conventional flake powders, e.g., Novamet HCA-1. The AB_5 hydrogen storage alloy (MH) was mixed with the flake copper or nickel powder in a weight ratio of Cu(Ni)/MH=0.2 using a mechanofusion machine (Hosokawa Micron Co. Ltd. AM-15F), which resembles a rotary ball mill. The mixture was press-bound on an expanded nickel mesh to form a metal hydride electrode which contained 1.68 g of the alloy. The electrochemical properties were tested in a MH-limited open cell using 6 M KOH in which the MH electrode was sandwiched between two nickel

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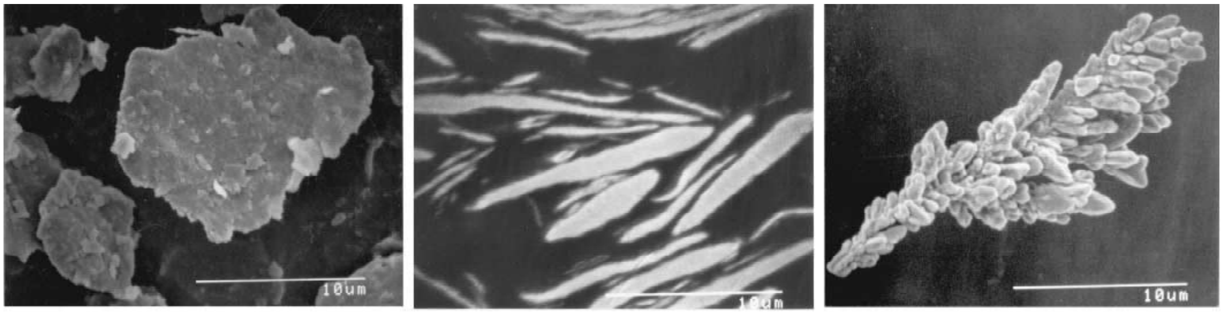


(a) Surface (b) Cross section (c) Conventional dendritic copper powder

Fig. 1. SEM photographs of conductive flake nickel powder and conventional dendritic copper powder.

electrodes. The cell was charged at 400 mA/g for 4 h, rested for 0.5 h, and then discharged at 400 mA/g down to 0.8 V. The AB_2 type alloy was mixed with the copper powder in the ratios of Cu/MH=0.5 and 3.0. Then the mixture was compacted to a pellet (10 mm in diameter) at 196 MPa and sandwiched with a nickel mesh current collector. The MH electrode was charged in 6 M KOH for 4 h at 100 mA/g, rested for 0.5 h, and discharged at 100 mA/g to −0.65 V vs. Hg/HgO reference electrode at 293 K. Metallographic examinations were performed by using a scanning electron microscope (SEM) and an electron probe microanalyzer (EPMA).

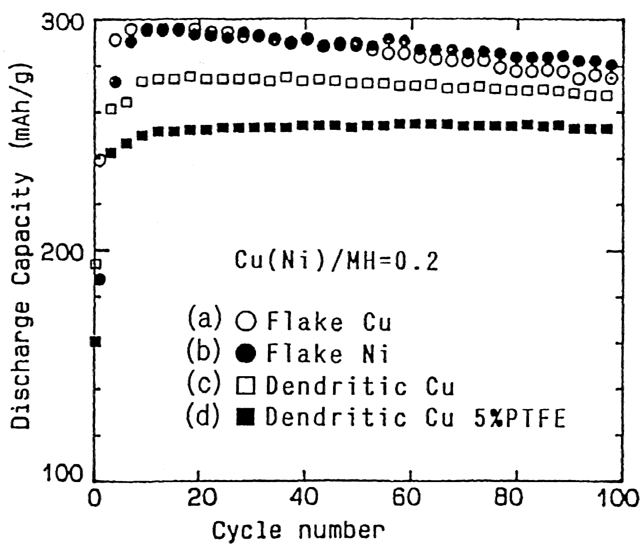
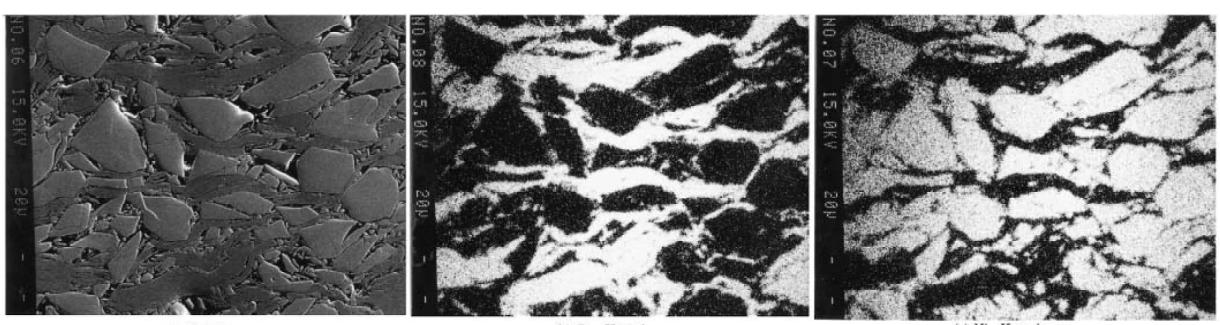


Fig. 2. Discharge capacity vs. cycle number curves for metal hydride electrodes (AB_5-type alloy) made with dendritic and flake powder of Cu and Ni.

3. Results and discussion

Fig. 2 shows the discharge capacity vs. cycle number curves at 293 K for various metal hydride electrodes (AB_5 alloy), electrode (a) made with flake copper powders (98 MPa pressing), electrode (b) made with flake nickel powders (294 MPa pressing), electrode (c) made with dendritic copper powders (98 MPa pressing), and electrode (d) made with dendritic copper powders and 5 wt.% polytetrafluoroethylen (PTFE). It is clear that the shape of the metal powder grains, dendritic vs. flake, and the presence of binding polymer (PTFE) greatly influences the dischargeable capacity of the electrodes. The electrode (c) made only with the dendritic copper powder shows a higher discharge capacity than that of (d) made with both the dendritic copper powder and PTFE binder. A further increase in the discharge capacity was achieved for the electrodes (a) and (b) made with flake copper and flake nickel powders. SEM and EPMA images on the cross-section of the MH electrodes using the flake copper powder are shown in Fig. 3. One can see that a lamellar-type network structure is formed, connecting the flake



(a) SEM image (b) Cu−K α image (c) Ni−K α image

Fig. 3. EPMA image of cross section of metal hydride electrodes (AB_5-type alloy) with flake copper powders.

powder particles to each other in the electrode. The micro-network structure improves the electrical conductivity, consequently increasing the utilization efficiency of hydrogen storage alloy.

Fig. 4 compares the initial discharge capacity of AB_2 type electrodes made with dendritic and flake copper powders in the Cu/MH ratio of 0.5 and 3.0 at 196 MPa pressing. A lowering of the Cu/MH ratio from 3.0 to 0.5 caused a significant decrease in the utilization efficiency of the alloy for dendritic copper powder. On the other hand, the electrode made with the flake copper powder showed a much higher capacity at the same Cu/MH ratio.

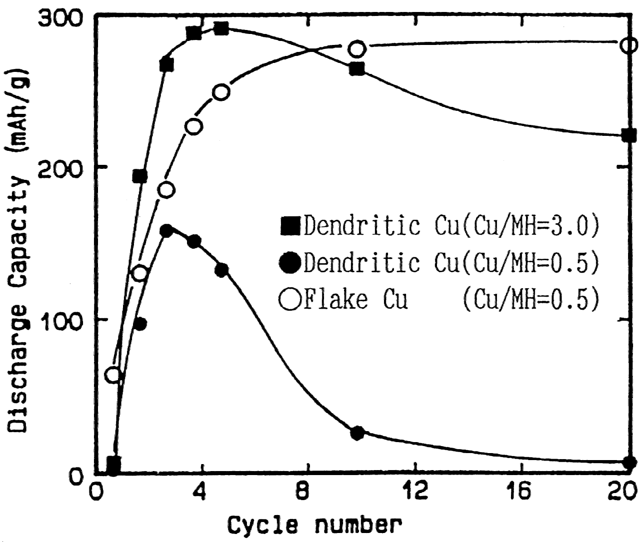


Fig. 4. Discharge capacity of AB_2-type alloy electrodes prepared by being pressed with dendritic and flake copper powders at 196 MPa.

4. Conclusions

The newly developed flake copper and nickel powders forms a laminated network structure which provides good conduction paths in the electrode and consequently improves the utilization efficiency of the alloy.

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