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A Study on the Electrode Characteristics of a New High Capacity Non-Stoichiometry Zr-Based Laves Phase Alloys for Anode Materials of Ni/MH Secondary Battery

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Abstract

For the purpose of developing the non-stoichiometric Zr-based Laves phase alloy with higher capacity and better performance for electrochemical application, extensive work has been carried out in KAIST. After careful alloy design of $ZrMn_2$-based hydrogen storage alloys through varing their stoichiometry while susbstituting or adding some alloying elements, the Zr-Ti-$(Mn\text{-}V\text{-}Ni)_{2.2}$, Zr-Ti-$(Mn\text{-}V\text{-}Cr\text{-}Ni)_{1.8\pm0.1}$ with high capacity and better performance was developed. Consequently the Zr-Ti-$(Mn\text{-}V\text{-}Ni)_{2.2}$ alloy has a high discharge capacity of 394 mAh/g and shows a high rate capability equaling to that of commercialized AB_5 type alloys. On the other hand, in order to develop the hydrogen storage alloy with higher discharge capacity, the hypo-stoichiometric $Zr(Mn\text{-}V\text{-}Ni)_{2-\alpha}$ alloys substituted by Ti are under developing. As the result of competitive roles of Ti and stoichiometry(α), the discharge capacity of Zr-Ti-$(Mn\text{-}V\text{-}Cr\text{-}Ni)_{1.8\pm0.1}$ alloys is about 400 mAh/g(410 mAh/g, which shows the highest level of performance in the Zr-based alloy developed. Our sequential endeavor is improving the shortcoming of Zr-based Laves phase alloy for commercialization, i.e., poor activation property and low rate capability, etc. It is therefore believed that the commercialization of Zr-based Laves phase hydrogen storage alloy for Ni-MH rechargeable battery is in near future.

1. Introduction

Nickel-metal hydride (Ni-MH) batteries using hydrogen storage alloys as negative electrodes have been developed and commercialized to meet the strong market demand for a power source with high energy density, high rate capability, long cycle life, and good environmental compatibility. In order to improve further the energy density of Ni-MH batteries, Zr-based Laves alloys should replace the commercial $MmNi_5$-type alloys, which have already reached their energy density limitations.

In this paper, the non-stoichometric Zr-based alloy is designed to have a higher discharge capacity and a better performance for the anode material of Ni/MH battery. Furthermore, the new activation treatment is investigated to apply for proto-type Ni/MH battery using the developed alloys. Finally the performance of proto-type 80Ah Ni/MH battery using the developed alloys is evaluated

2. Experimental details

The base alloy was prepared in an arc-melting furnace under an argon atmosphere. The samples were crushed and ground into a powder with a characteristic particle diameter of about 100μm for measurement of P-C-Isotherms and a particle diameter less than 45μm for electrochemical measurements. For the electrochemical measurement, electrodes were made by mixing the sieved powders with nickel powder in a weight ratio of 1:3 and pressing this mixtures at a pressure of 10^4 N/m^2 to porous pellets having a diameter of 10 mm. The experimental cell for electrochemical measurements consisted of the working electrode (Metal Hydride electrode), the counter electrode (Pt wire) and a reference electrode (Hg/HgO electrode). The electrolyte was 30 wt% KOH solution and its temperature was controlled at 30$\pm$ 1°C. The alloy electrode was galvanostatically charged at 100 mA/g for 6h, and after resting for 5min it was discharged at 100 mA/g until the potential reached -0.75 V vs. Hg/HgO. To examine the reason for the change of discharge behavior of electrode through alloy design, the electrochemical(E.I.S., Linear polarization method, etc.) and phenomenological (S.E.M., E.D.S., A.E.S., I.C.P., etc.) analyses were performed.

3. Results and discussion

3.1. Design of Hypo-stoichiometric Zr-based alloy for higher discharge capacity

After careful design of Zr-Mn-Ni alloy, $Zr(Mn_{0.2}V_{0.2}Ni_{0.6})_{1.8}$ alloy reveals relatively good properties in view of hydrogen storage capacity, hydrogen equilibrium pressure and electro-

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chemical discharge capacity. In order to improve the discharge capacity and rate-capability, Zr is partially substituted by Ti. The discharge capacity at 30°C for $Zr_{1-X}Ti_X$ $(Mn_{0.2}V_{0.2}Ni_{0.6})_{1.8}$ (X=0.0, 0.2, 0.4, 0.6) alloy electrodes passes through a maximum with Ti content in the alloys. In view of electrochemical and thermodynamic characteistics, the maxima phenomenon of the electrochemical discharge capacity of the alloy is attributed to a competition between decreasing hydrogen storage capacity and increasing of rate-capability with increasing Ti content. However, as Ti mole fraction increases, the discharge capacity decreases more rapidly with repeated electrochemical cycling. Judging from the analysis of surface composition by A.E.S., the rapid degradation with increasing Ti content in Zr-based alloy is ascribed to the fast growth of the oxygen-penetrated layer with cycling. Therefore, we can assure that the stoichiometry and Ti content should be optimized to insure the good cycle performance of electrode. On the basis of above results, extensive works have been carried out on developing the hypo-stoichiometric Zr-based alloy with higher discharge capacity maintaining good cycle performance. Consequently, the hydrogen storage capacity of $Zr_{0.7\pm X}Ti_{0.3\pm X}(Mn_aV_bCr_cNi_{1-a-b-c})_{1.8\pm Z}$ alloys with optimized composition is about 1.68 wt% under 10atm as shown in Fig. 1, and the discharge capacity of the alloy is about 400 mAh/g(410 mAh/g, which shows the highest level of performance in the Zr-based alloy developed (Fig. 2).

3.2. Design of Hyper-stoichiometric Zr-based alloy for higher discharge capacity

After some careful selection of $ZrMn_2$ Laves phase alloys to have suitable hydrogen equilibrium pressure and to be discharged in KOH solution, the $ZrMn_{0.5}V_{0.5}Ni_{1.4}$ alloys meet the above requirements reasonably well. The hydrogen storage performance and discharge characteristics of $ZrMn_{0.5}V_{0.5}$

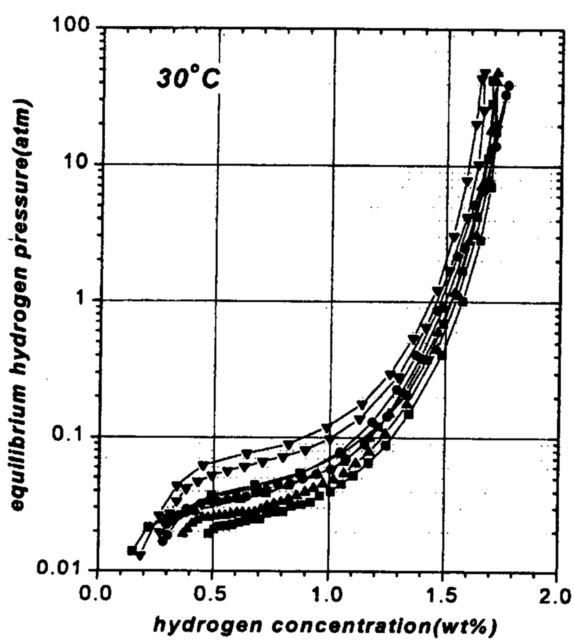

Fig. 1. The P-C-T curves of various hypo-stoichiometric Zr-based alloy with optimized composition.

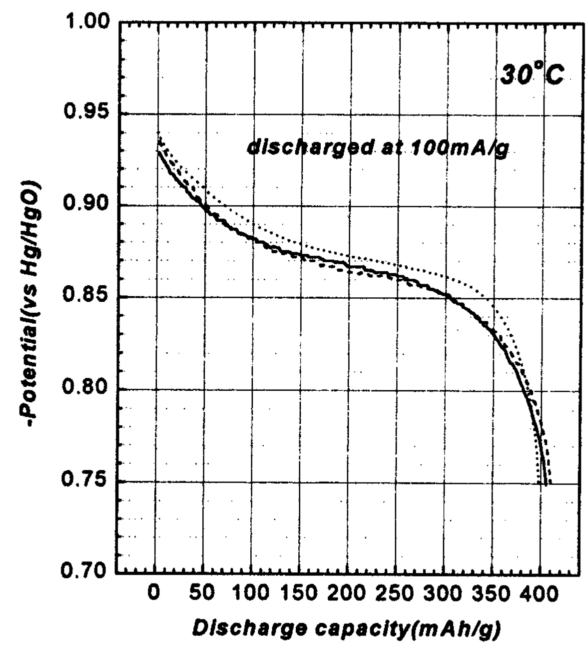

Fig. 2. The discharge curves of various hypo-stoichiometric Zr-based alloy with optimized composition.

$Ni_{1.4+y}$ (y=0.0, 0.2, 0.4 and 0.6) alloys is determined for variable Ni content, which is believed to have some influence on the rate-capability. As the Ni content in the alloy increase, the hydrogen storage capacity decrease and the hydrogen equilibrium pressure increase. However, it is unexpectedly found that the rate-capability of these alloys decreased with increasing Ni content. The decrease of reaction surface area with increasing Ni content in this alloy explains that the major factor affecting the rate-capability is the reaction surface area and not the specific surface catalytic activity. After comparison of discharge characteristics such as discharge capacity and rate-capability of $ZrMn_{1-x}V_xNi_{1.4+y}$ (x = 0.5, 0.7; y = 0.0, 0.2, 0.4 and 0.6) for variable Mn to V ratio, it is found that the more Mn rich alloy showed higher rate capability due to a larger reaction surface. On the basis of the above results, the alloy composition was optimized for a Mn to Ni ratio of 0.7 : 1.2, i.e. for $ZrMn_{0.7}V_{0.5}Ni_{1.2}$. In order to increase the discharge capacity of the $ZrMn_{0.7}V_{0.5}Ni_{1.2}$ alloy, Ti is partially substituted for Zr and the stoichiometry is also changed. This change also increases the rate-capability. After such careful alloy design reached by substitution and changing stoichiometry, $Zr_{0.9}Ti_{0.1}(Mn_{0.29}V_{0.21}Ni_{0.50})_{2.2}$ alloys with high capacity and high rate-capability have been developed. This alloy has a discharge capacity of 394 mAh/g at 0.25C discharge rate (Fig 3) and shows high rate-capability (92% at 1C rate) equaling that of commercialized AB5 type alloys (Fig. 4).

3.3. The activation treatment for full-cell system (proto-type Ni/MH battery)

In order to improve the activation properties of Zr-based alloy electrode, the various treatments such as a KBH_4 treatment, a pulse-charging and a hot-charging treatment have been suggested. However, these proposed treatments were

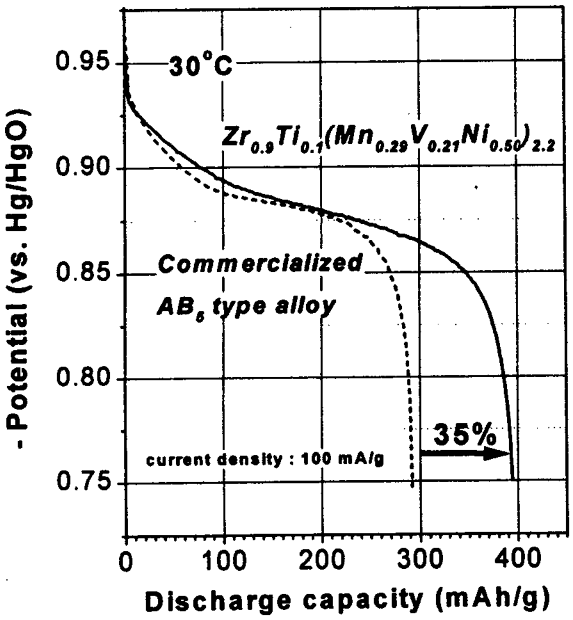

Fig. 3. Discharge curves of $Zr_{0.9}Ti_{0.1}(Mn_{0.29}V_{0.21}Ni_{0.50})_{2.2}$ and commeriallized $Mm(Ni\text{-}Co\text{-}Al\text{-}Mn)_5$ alloys at 30°C.

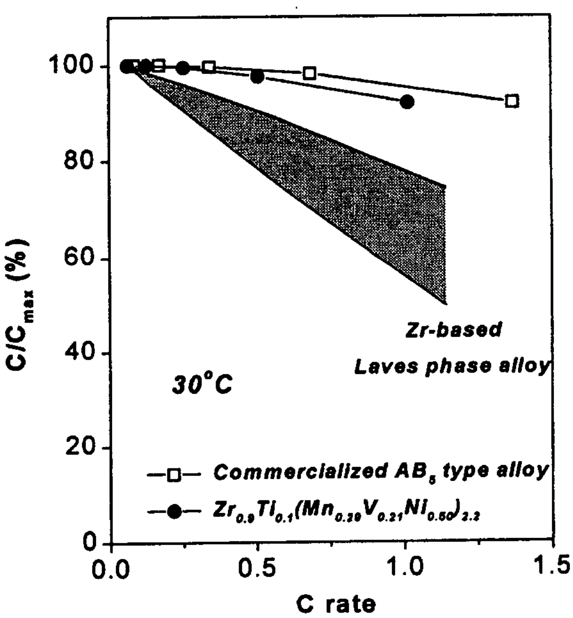

Fig. 4. Rate capability of $Zr_{0.9}Ti_{0.1}(Mn_{0.29}V_{0.21}Ni_{0.50})_{2.2}$ and commeriallized $Mm(Ni\text{-}Co\text{-}Al\text{-}Mn)_5$ alloys at 30°C.

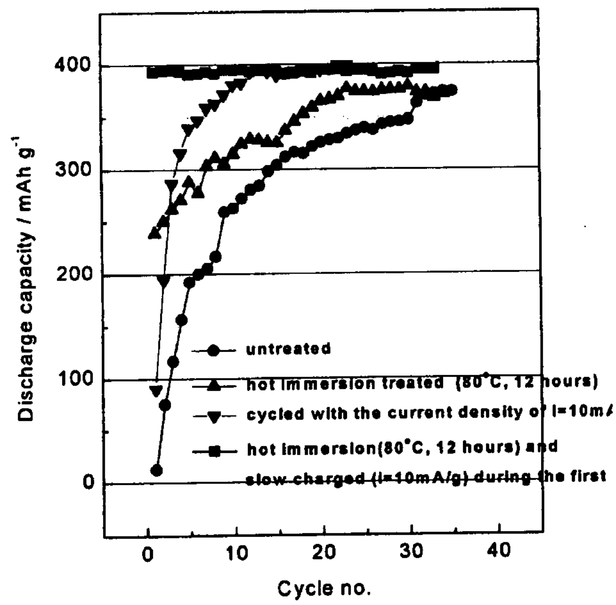

Fig. 5. The activation behaviours of Zr-based alloy electrode after various treatments.

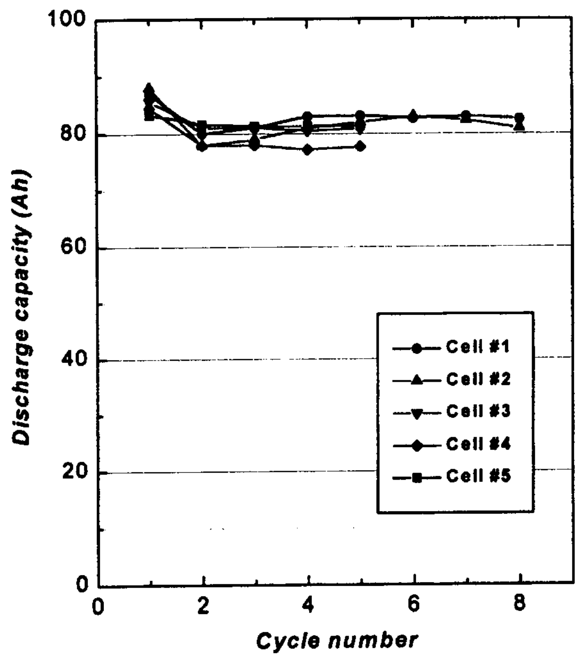

Fig. 6. The activation behaviours of proto-type 80Ah cells after hot-immersion and slow-charging treatments.

not satisfactory in a view of avoiding the overcharge of $Ni(OH)_2$ electrode or applying the formation process of the Ni/MH battery. In this work, the effects of combination of the hot-immersion and the slow-charging method on the activation of the $Zr_{0.9}Ti_{0.1}(Mn_{0.29}V_{0.21}Ni_{0.50})_{2.2}$ alloy is investigated.

The $Zr_{0.9}Ti_{0.1}(Mn_{0.29}V_{0.21}Ni_{0.50})_{2.2}$ alloy electrode is completely activated at the first cycle when the electrode is immersed at 80°C for 12hr in a KOH solution and then charged at the current density of 10 mA/g (Fig. 5). It is believed that the improved activation behavior of the electrode is attributed to the synergic effect between the hot immersion and slow-charging method. The hot-immersion treatment is a useful method for the activation of the alloy by removing the surface oxide layer. The slow-charging also facilitates an easier hydrogen absorption of the alloy. When the electrode is immersed in a hot KOH solution and then charged slowly, the hydrogen penetrates more easily into the inner part of the alloy without having obstacles and the new clean surface can be formed easily.

3.4. The performances of proto-type 80Ah Ni/MH battery fabricated in KAIST

The sealed 80 AH Ni-MH battery is fabricated for EV system in KAIST. The fabrication method of paste-type electrode was established by adopting Cu powder as an additive material for improving the performance of MH anode. For initial activation of battery, new activation process was developed, which was applied to the battery, resulting in being activated within 1-2 cycle (Fig. 6). Finally, we have developed 80 Ah Ni/MH cells with better performances than conventional EV cell which adopted AB_5 type alloy as a anode material and high energy density, equaling to that of the conventional EV cell.

4. Conclusions

Zr based Laves alloys should replace the commercial $MmNi_5$-type alloys which have already reached their energy density limitations, judging from their hydrogen storage capacity. However, to utilize Zr-based alloy as a electrode material, some characteristics such as activation, rate capability, discharge capacity should be improved.

• The careful design of hypo-stoichiometric alloys result in developing $Zr_{0.7\pm X}Ti_{0.1\pm X}(Mn_aV_bCr_cNi_{1-a-b-c})_{1.8\pm Z}$ (X<0.1, Z<0.1) with higher discharge capacity of 400-410 mAh/g, which is the highest level in performance of Zr-based alloys developed.

• We have developed $Zr_{0.9}Ti_{0.1}(Mn_{0.29}V_{0.21}Ni_{0.50})_{2.2}$ alloy with good rate capability (92% at 1C rate) equaling to that of the commercial AB_5 type alloy maintaining high discharge capacity (394 mAh/g)

• The Zr-based alloy is fully activated within 1 cycle by applying the new activation treatment, which is found to be successfully applicable to the Ni/MH battery system.

• With the non-stoichiometric Zr-based alloy developed, we have developed 80 Ah Ni/MH cells with better performance than conventional EV cell and high energy density, equaling to that of the conventional EV cell

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