

Short Communication

## Charging efficiency of metal-hydride electrodes

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### Abstract

The charging efficiencies of  $MmNi_5$ ,  $MmNi_{4.5}Mn_{0.5}$ ,  $MmNi_{3.8}Co_{0.7}Mn_{0.5}$ ,  $ZrV_{0.6}Ni_{1.4}$ ,  $ZrV_{0.6}Mn_{0.4}Ni_{1.0}$ ,  $ZrV_{0.6}Mn_{0.4}Co_{0.2}Ni_{0.8}$  alloy electrodes (Mm = Mischmetal) are investigated in terms of hydrogen evolution. Experiments are conducted to optimize: (i) elemental composition of the  $MmNi_5$  system and Zr-based Laves-phase hydrogen storage alloys; (ii) additive materials, such as cobalt powder, nickel powder, Teflonized carbons, and acetylene black; (iii) the proportion of the additives in the alloy; (iv) the best percentage of the composite additives in the metal-hydride electrodes. The results show that the electrode activation, charging efficiency and high-rate discharge depend greatly on the active materials, as well as the type and the amount of the additives in the electrodes. © 1998 Elsevier Science S.A.

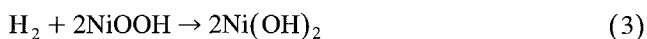
*Keywords:* Metal hydride electrodes; Additives; Charging efficiency

### 1. Introduction

Recent studies [1,2] show that nickel/metal-hydride (Ni/MH) batteries have attracted attention because they are more environmentally acceptable, have higher specific energy and higher charge-rate capability compared with nickel/cadmium (Ni/Cd) batteries. To develop practical Ni/MH batteries, however, the capacity decay and the high internal pressure of sealed units must be overcome [3,4]. The main causes for these problems are: (i) deterioration of the metal-hydride electrodes caused by pulverization and passivation of the alloy, and disintegration of the electrode; (ii) leakage of electrolyte under the high internal pressure caused by the low charging efficiency after repeated charge/discharge cycles.

The internal pressure of a sealed Ni/MH battery is controlled by many factors. For example, it is well known that hydrogen evolution (Eqs. (1) and (2)), which is produced by side reactions at the MH electrode, leads to a lowering of the charging efficiency [5]. The consumption rate of hydrogen according to Eq. (3) is relatively slow, so that a significant increase in battery pressure is created in a sealed Ni/MH battery. Thus, to achieve a sealed battery, it is very important to prevent the side reaction of hydrogen evolution. A study by Ogawa et al. [6] has indicated that the  $MmNi_5$  system alloy is widely used for the MH electrode because of its good performance. Nevertheless, evaluation of the charging efficiency of Zr-based Laves-

phase alloy has not been reported. Moreover, both the type and the amount of the additives required in the process of making the MH electrode have not been determined and disagreement exists in the literature [7,8]. Petrov et al. [9] reported that additives such as Teflonized carbon (TC) or acetylene black (AB) form a flexible, three-dimensional network which provides an intimate and a stable contact between the active alloy particles. Sakai et al. [5] found that a large amount of hydrogen was produced in a cell that contained up to 20 wt.% of Ni or Cu powder, additives and, thereby, caused a gradual rise in pressure during repeated charge/discharge cycles.



This study examines the properties of MH electrodes using: (i) a  $MmNi_5$  system and Zr-based Laves-phase alloys; (ii) different additive materials such as Co powder, Ni powder, TC, and AB; (iii) various amounts of these additive materials in the alloy electrodes.

### 2. Experimental

The  $MmNi_5$  (alloy A),  $MmNi_{4.5}Mn_{0.5}$  (alloy B),  $MmNi_{3.8}Co_{0.7}Mn_{0.5}$  (alloy C),  $ZrV_{0.6}Ni_{1.4}$  (alloy D),

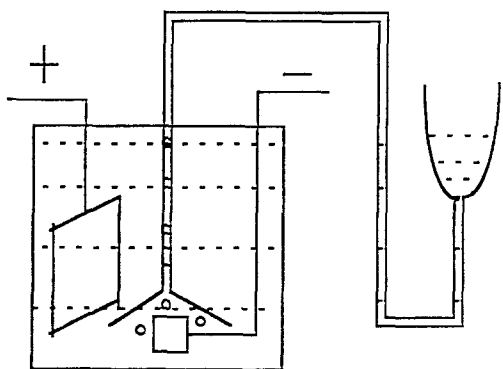


Fig. 1. Schematic of the apparatus for examining the charging efficiency.

ZrV<sub>0.6</sub>Mn<sub>0.4</sub>Ni<sub>1.0</sub> (alloy E), ZrV<sub>0.6</sub>Mn<sub>0.4</sub>Co<sub>0.2</sub>Ni<sub>0.8</sub> (alloy F) alloy samples were prepared by arc-melting of the components (Mm is Mischmetal in the weight ratio of La:Ce:Pr:Nd = 60:30:3:6) with a purity of more than 99.5 wt.% under argon atmosphere, followed by annealing at 1050 °C for 10 h. The alloys were then crushed and ground mechanically into powders with a particle size smaller than 78 μm.

The MH electrodes were prepared by intimately mixing: (i) the above alloys with 25 wt.% Ni powder; (ii) alloy C or alloy F with 25 wt.% composite material (Ni, Co, TC, or AB powder); (iii) different ratios of the additive material and alloy C. Polyvinyl alcohol solution (3 wt.%) was added to the mixture as a binder. The mixture was then filled into a nickel-foam matrix, followed by drying and pressing at  $2 \times 10^7$  Pa. The geometric dimensions of the electrodes were  $2 \times 2 \times 0.06$  cm.

The electrochemical cell consisted of the MH working electrode, an NiOOH/Ni(OH)<sub>2</sub> counter electrode, and a Hg/HgO reference electrode. All potentials are reported with respect to this reference electrode. The electrolyte was 6 M KOH solution and the temperature was controlled at  $25 \pm 1$  °C. The electrode properties were measured with an automatic galvanostatic charge/discharge unit (DEC-1). When discharged, a maximum potential of -600 mV was adopted as a standard for these series of tests. The evolution of hydrogen and the charging efficiency were tested using the equipment shown in Fig. 1. The electrodes were activated as follows: charged at 30 mA for 7.5 h and discharged at 30 mA to -600 mV.

### 3. Results and discussion

#### 3.1. Electrode activation

The results of the activation experiments of A, B, C, D, E and F electrodes are shown in Fig. 2 as a graph of electrode capacity versus cycle number. The results show that after 5 charge/discharge cycles, the A, B, C alloy electrodes obtain their highest discharge capacity, which is

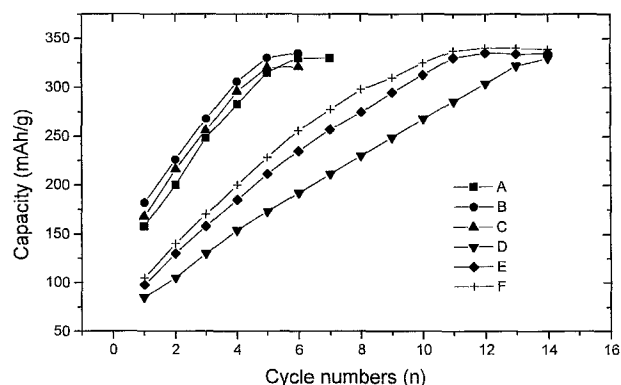


Fig. 2. Activation of metal-hydride electrodes.

328, 335, 320 mAh g<sup>-1</sup>, respectively. By contrast, it took more than 12 cycles for the D, E, F alloy electrodes to reach their highest capacity, namely, 310, 330, 345 mAh g<sup>-1</sup>, respectively.

#### 3.2. Capacity at different discharge current densities

The capacities of the above electrodes at different discharge current densities are listed in Table 1. The results reveal that: (i) at the lowest discharge rate (50 mA g<sup>-1</sup>), the discharge capacities of all electrodes are almost the same; (ii) the higher the discharge rate, the larger the difference between the electrode capacities, for example, alloys C and D exhibit, respectively, the highest and lowest discharge capacity at a discharge current density of 300 mA g<sup>-1</sup>; (iii) MmNi<sub>5</sub> system alloys have better high-rate discharge abilities than those of the Zr-based Laves-phase alloys and also, for each system, the addition of Mn or Co greatly improves this property. Previous work by Zhang et al. [10] has demonstrated that at low discharge current density, the charge/transfer process is the dominant electrode reaction; whereas at a high discharge current density, hydrogen diffusion within the bulk alloy is the rate-determining step. The above results confirm that addition of Mn or Co to the alloys has an important electrocatalytic effect; it prevents the release of hydrogen gas from the alloy surface and suppresses the recombination of hydrogen atoms and facilitates their diffusion into the alloy.

Table 1  
High-rate discharge capacities

Discharge current density (mA g <sup>-1</sup> )	Discharge capacity (mAh g <sup>-1</sup> )					
	A	B	C	D	E	F
50	328	335	325	310	330	345
100	286	298	300	242	258	268
300	242	252	260	178	204	209
<i>C</i> <sub>300</sub> / <i>C</i> <sub>50</sub>	0.738	0.752	0.8	0.574	0.618	0.606

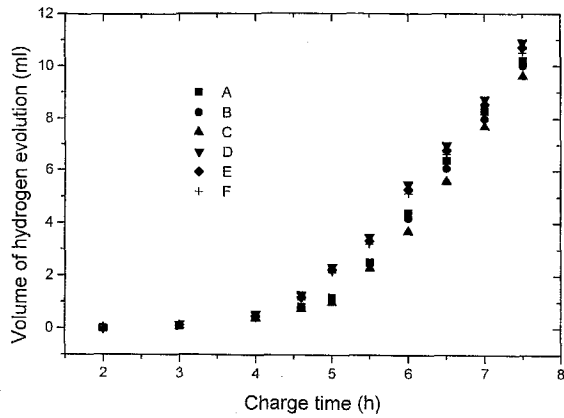


Fig. 3. Hydrogen evolution on charged metal-hydride electrodes.

3.3. Effect of different active materials on hydrogen evolution

In order to determine the charging efficiency of the above electrodes, the hydrogen evolution on these electrodes was measured during charging. The relation between the volume of hydrogen evolved and the charging time is shown in Fig. 3. It can be seen that at the end of charging, there is a linear relationship. When this line is extended to intersect with the time line at  $t_c$ , it shows the time at which large amounts of hydrogen start to evolve. Thus,  $t_c$  can be considered to be the efficient charging time. Thus, the efficient charged capacity,  $C_{ec}$ , equals  $It_c$ . After the electrodes were charged, they were discharged directly, in order to avoid self-discharge. If the discharge capacity is  $C_{dis}$ , then the charging efficiency  $\eta$  is defined by the following equation

$$\eta = (C_{ec} C_{dis}^{-1}) \times 100\% = (It_c C_{dis}^{-1}) \times 100\% \quad (4)$$

The effects of active materials on the charging efficiency are summarized in Table 2. The data show that the charging efficiencies are in the order:  $\eta_C > \eta_B > \eta_A > \eta_F > \eta_E > \eta_D$ .

3.4. Effect of different additive materials on hydrogen evolution

Alloys C and F were selected to investigate the effect of additive materials on the charging efficiency of the metal-hydride electrodes. The results are summarized in Table 3.

Table 2  
Charging efficiencies

Electrode	A	B	C	D	E	F
$I$ (mA)	25	25	25	25	25	25
$t_c$ (h)	4.89	4.93	4.96	4.70	4.78	4.85
$C_{dis}$ (mAh)	127	126	126	127	128	129
$\eta$ (%)	96.2	97.8	98.4	92.5	93.4	94

Table 3  
Effect of additives on charging efficiency of electrodes C and F

Additives:	Co		Ni		TC		AB	
Electrodes:	C	F	C	F	C	F	C	F
$I$ (mA)	25	25	25	25	20	20	20	20
$t_c$ (h)	4.96	4.86	4.91	4.83	4.78	4.72	4.70	4.66
$C_{dis}$ (mAh)	126	129	126	129	103	103	102	103
$\eta$ (%)	98.4	94.2	97.4	93.6	92.8	91.6	92.2	90.5

The charging efficiencies of electrodes C and F are in the same order, namely:  $\eta_{Co} > \eta_{Ni} > \eta_{TC} > \eta_{AB}$ . It would appear that Co or Ni are the most active electrocatalysts for MH electrodes. Previous work [11] has concluded that electrochemical reaction sites at the MH electrodes are located on the alloy surface which has a high catalytic activity that is comparable with that of platinum. The fact that Co or Ni powder has a smaller effect on the hydrogen evolution supports this conclusion. If the hydrogen atoms produced on the alloy surface diffuse rapidly through the outside layer of the alloy and then form a hydride, the hydrogen evolution will be prevented. As a result, the rapid pressure rise will be hindered, and the charging efficiency will be improved.

3.5. Effect of additive material content on properties of MH electrodes

The effect of the amount of all the studied additive materials on the capacity of the alloy C electrode is shown in Fig. 4. The results are similar for all the additive materials. As the amount of additive is increased to 25–30 wt.%, the capacity rises to a maximum as the electronic conductivity of the electrode increases. On the other hand, as the amount of additive material is increased further, all electrodes show a gradual fade in capacity as the proportion of active material in the electrode is diminished. The

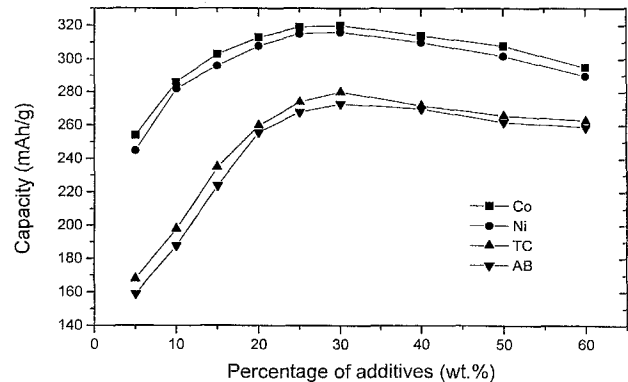


Fig. 4. Correlation of electrode capacities with percentage of additive materials.

Table 4  
Effects of composite additives (25 wt.%) on charging efficiency

Composite additives	Co+Ni	Co+Ni+TC	Co+Ni+TC+AB	TC+AB
$I$ (mA)	25	25	22	20
$t_c$ (h)	4.97	4.95	4.93	4.74
$C_{dis}$ (mAh)	126	126	112	104
$\eta$ (%)	98.6	98.2	96.8	91.2

decrease in capacity at low contents is probably due to a decrease in electronic conductivity.

### 3.6. Effect of composite additive material content on hydrogen evolution

In the manufacturing process of an MH electrode, two aspects should be considered, namely, good electrode properties and low cost. Because Co powder is very expensive, its content in an electrode should be as low as possible. Accordingly, the following work focuses on the effect of the composite additive materials on the charging efficiency of the electrode. The ratio of the additive to the materials (alloy) was held constant (25 wt.%), but the ratio Co:Ni:TC:AB was varied (Table 4). The electrode with Co powder, Ni powder and TC has a charging efficiency of 98.2%, which means that hydrogen evolution is greatly depressed. If this electrode is used in a sealed Ni/MH battery, the internal pressure caused by hydrogen would be lowered.

## 4. Conclusions

When Ni in the  $MmNi_5$  and  $ZrV_{0.6}Ni_{1.4}$  alloy is partially substituted by Mn and Co, an enhanced activation and a high-rate discharge is obtained. For the  $MmNi_5$  system alloy, the electrode activation is faster, the high-rate discharge is better, and the charging efficiency is higher than that of the Zr-based Laves-phase alloy. The charging

efficiency ( $\eta$ ) of electrode C is in the order of  $\eta_{Co} > \eta_{Ni} > \eta_{TC} > \eta_{AB}$  when Co powder, Ni powder, TC or AB is used as the additive material, respectively. The electrode with 25 wt.% of composite additive materials (Co, Ni and TC) exhibits a charging efficiency of 98.2%. This is probably due to the fact that the additives catalyse the chemical reaction of  $H_2O + e^- \rightleftharpoons H + OH^-$  and facilitates the diffusion of hydrogen through the alloy.

## Acknowledgements

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