

Modification of $\text{Ti}_{0.35}\text{Zr}_{0.65}\text{Ni}_{1.2}\text{V}_{0.6}\text{Mn}_{0.2}$ alloy powder by electroless nickel coating and its influence on discharge performance

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Abstract

The electrochemical performance of an AB_2 -type hydrogen storage alloy ($\text{Ti}_{0.35}\text{Zr}_{0.65}\text{Ni}_{1.2}\text{V}_{0.6}\text{Mn}_{0.2}$) modified by electroless Ni–P and Ni coatings in acid hypophosphite and hydrazine baths, respectively, is investigated. It is found that electrochemical properties of the modified electrodes (i.e., high-rate dischargeability, cycle life, ability to retain discharge capacity after overdischarge) and the electrocatalytic activity for the hydrogen electrode reaction are improved by this surface modification. The high-rate dischargeability of the alloy coated with Ni from the hydrazine bath is better than that coated with Ni–P from the acid hypophosphite bath, but the activation cycles required for the Ni-coated electrode to reach maximum capacity are four times as many as those required by the electrode coated with Ni–P. A duplex nickel coating method has therefore been developed. The duplex nickel-coated alloy (i.e., alloy first coated with Ni–P and then coated with Ni) retains the characteristics of better high-rate dischargeability but requires fewer activation cycles in comparison with the Ni-coated alloy.

Keywords: Hydrogen storage alloy; Electroless nickel coating; Discharge; Alloys

1. Introduction

With the increasing demand for power sources that offer high specific energy, high-rate capability, long cycle-life and low environmental impact, rechargeable metal hydride batteries have become very important.

Two types of alloys, the AB_5 -type (rare earth-based) [1] and AB_2 -type Laves phase alloy (titanium-based or zirconium-based) [2,3], have been employed extensively as electrode materials. A previous communication has reported [4] a promising AB_2 -type Laves phase alloy ($\text{Ti}_{0.25}\text{Zr}_{0.65}\text{Ni}_{1.2}\text{V}_{0.6}\text{Mn}_{0.2}$) with large hydrogen storage capacity and good reversibility for desorption. On the other hand, its cycling performance is still poor.

The dischargeability of metal hydride electrodes can be manipulated by adjusting the composition of the hydrogen storage alloy [5,6]. During cycling in KOH electrolytes, Ti and Zr components that act as the main hydrogen storage components tend to form thermodynamically stable oxides. The oxide layer blocks the surface of the alloy and decreases the catalytic activity of the electrodes. The catalytic activity of the electrode surface is one of the major factors that affect the high-rate dischargeability and activation behaviour of the

electrodes. Modification of the LaNi_5 -based alloy electrodes by electroless Cu, Ni–P, Ni–B coatings has been found to be very effective in improving the high-rate dischargeability [7,8] and in reducing the inner pressure of batteries during overcharge and overdischarge [9]. Micro-encapsulation of $\text{Zr}_{0.8}\text{Ti}_{1.2}\text{Ni}_{1.35}$ powders by electroless nickel or copper plating has also been found [10] to increase remarkably the durability of the electrode.

Although there are many reports concerning the effects of copper coating on the hydride/dehydride properties of alloys, studies of the performances of nickel-plated alloys are comparatively few. Electroless nickel plating is used extensively in engineering coatings because of its exceptionally high wear and corrosion resistance [11]. The properties associated with the nickel deposit depend on the microstructure which, in turn, is influenced by the extent of the co-deposited phosphorus (or boron). In this work, the modification effects of electroless nickel coating on $\text{Ti}_{0.35}\text{Zr}_{0.65}\text{Ni}_{1.2}\text{V}_{0.6}\text{Mn}_{0.2}$ electrodes are investigated in terms of high-rate chargeability and dischargeability, cycle life, and the protection of discharge capacity during overdischarge. Two types of nickel coating are explored, namely: Ni–P codeposition and Ni deposition free of phosphorus.

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2. Experimental

2.1. Surface modification of alloy powder and electrode preparation

Metals of 99.5% purity were used to prepare an alloy with a nominal formula of $Ti_{0.35}Zr_{0.65}Ni_{1.2}Mn_{0.2}V_{0.6}$. The metals were melted by an arc-melting method under an argon atmosphere. The ingot was turned over 14 times by cooling and remelting to ensure homogeneous quality. The powder (obtained through a 325 mesh sieve after mechanical pulverization) was activated by heating under a hydrogen atmosphere at 400 °C for 1.5 h. The hydrogen was removed at 400 °C and the powder was then cooled to room temperature. Finally, argon was introduced to prevent oxidation of the powder.

The activated powder was chemically coated with 25 wt.% electroless nickel. The chemical composition and operating conditions of the baths are given in Tables 1 and 2 [12]. The bath was continuously stirred at 83 ± 1 °C during the plating process. After plating, the powder was washed thoroughly with de-ionized water and then alcohol. The powder was finally filtered under reduced pressure.

Three types of electrodes were prepared. The first type (electrode A) was prepared by mixing bare alloy powder with 25 wt.% nickel powder and 3 wt.% polytetrafluorethylene (PTFE) dispersion. The second type (electrode B) was prepared by mixing Ni–P coated alloy powder with 3 wt.% PTFE dispersion. The third type (electrode C) was prepared by mixing pure nickel-coated alloy powder with 3 wt.% PTFE dispersion. The mixtures were compacted into square pellets

Table 1
Composition and operating conditions of nickel electroless plating baths with hypophosphite as a reducer

Composition	Content (g/l)
Nickel chloride ($NiCl_2 \cdot 6H_2O$)	30
Ammonium bifluoride ($NH_4F \cdot HF$)	20
Potassium acetate (CH_3COOK)	10
Trisodium citrate ($Na_3C_6H_5O_7$)	20
Sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$)	10
pH	6.9
Product	Ni–P coatings

Table 2
Composition and operating conditions of nickel electroless plating baths containing hydrazine as a reducer [12]

Composition	Content (g/l)
Nickel chloride ($NiCl_2 \cdot 6H_2O$)	24.7920
Potassium bicarbonate ($KHCO_3$)	45.0687
Hydrazine hydrate ($N_2H_4 \cdot H_2O$)	40.6738
Potassium carbonate (K_2CO_3)	69.1050
Potassium phosphate (K_2HPO_4)	87.0900
Potassium hydroxide (KOH)	13.1416
pH	11.5
Product	Ni coatings

(each with an apparent surface area of $2.5 \text{ cm} \times 2.5 \text{ cm}$) for discharge capacity measurements. A nickel net was sandwiched between the two alloy pellets under a pressure of 1 ton/cm². The electrodes thus formed with thickness of 1.0 mm were heated at 250 °C under vacuum for 20 min.

2.2. Electrochemical measurements

The cell comprised a working electrode made of a hydrogen storage alloy, a counter electrode ($Ni(OH)_2/NiOOH$), and a reference electrode (Hg/HgO electrode). The capacity of the counter electrode was much larger than that of the working electrode. The working electrode was wrapped in non-woven Nylon separator (Pellen 2516) and then inserted between two counter electrodes. The latter were held together tightly in a Teflon holder. Galvanostatic charge/discharge cycles were carried out in 30 wt.% KOH solution at 30 °C. The negative working electrode was charged for 15 h and discharged to -0.7 V (with respect to Hg/HgO electrode) at a constant current density of 25 mA/g. After charging, the cell was first left under open-circuit condition for 1 h and then discharged to -0.7 V . The discharge capacity of the negative electrode was also determined at constant current densities of 50, 100, 200 and 300 mA/g.

2.3. Examination of surface morphology and composition

The nickel-coated alloy powder was polished in order to study its microstructure. Surface morphology was characterized by means of a scanning electron microscope (SEM: JSM-840A) and an electron probe microanalyzer (EPMA: TCX-733). The concentration of elements dissolved in the plating baths and the content of nickel coated on the alloy powders were examined by inductively coupled plasma emission spectroscopy (ICP). The crystal structure of the modified alloy powder was identified by X-ray diffraction (XRD) with Cu $K\alpha$ radiation.

3. Results and discussion

3.1. Surface morphology and composition examination

Various studies [5,13,14] indicate that both the surface morphology and the composition of hydrogen storage alloys are very important for improving the electrocatalytic activity and the cycle life of negative electrodes.

The surface morphology of Ni–P coated alloy powder as observed by SEM and EPMA is displayed in Fig. 1. The elemental distribution of the Ni–P coated alloy powder determined by EPMA is shown as the mapping of the elements Ni (Fig. 1(b)) and P (Fig. 1(c)). The line profiles of Ni and P are shown in Figs. 1(d) and 1(e), respectively. The electron micrograph of the corresponding position for Fig. 1(b) and 1(c) is presented in Fig. 1(a). The outer part of the grain in

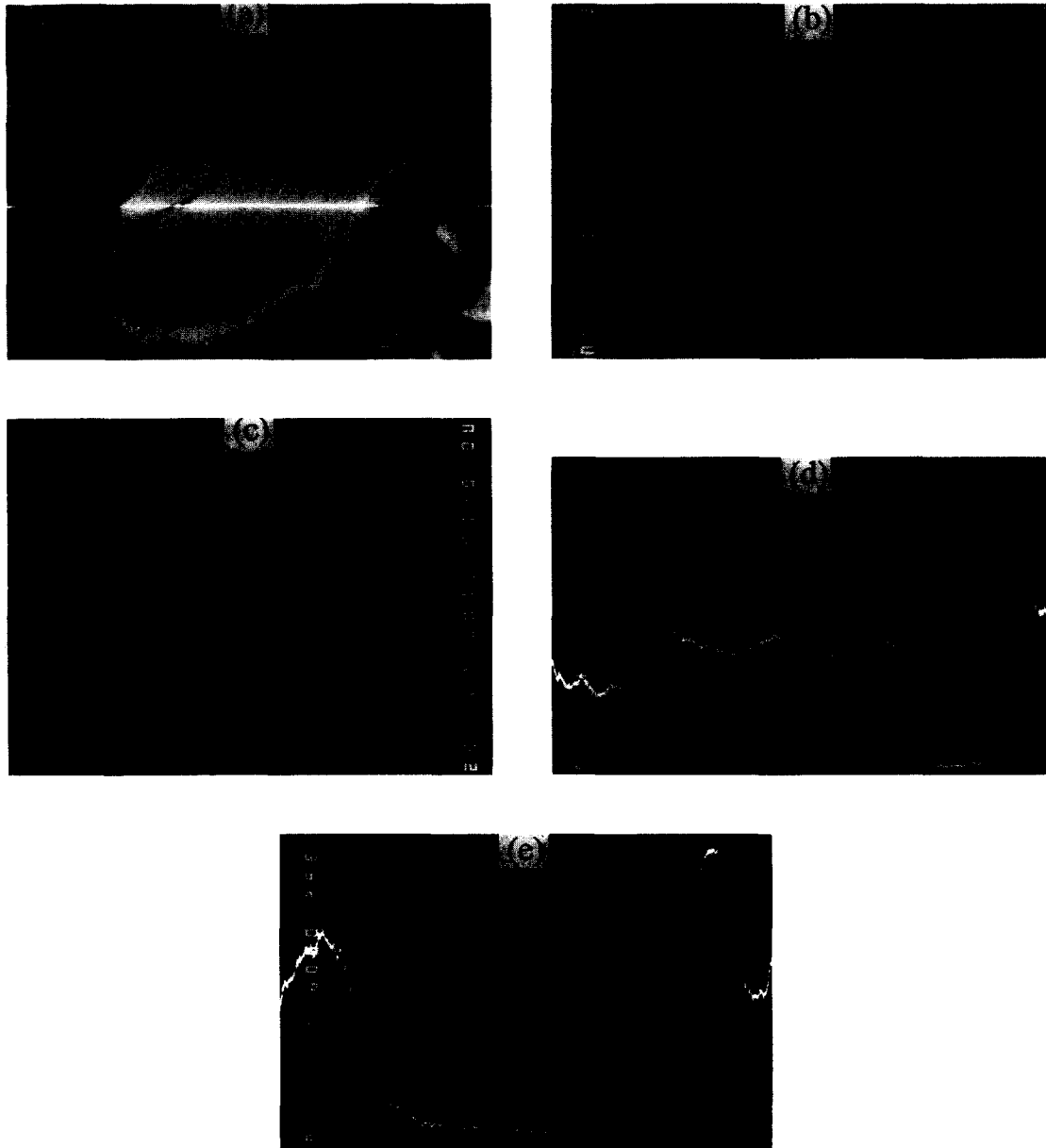


Fig. 1. Surface morphology of Ni–P coated alloy powders by SEM and EPMA. Line profiles of Ni and P are shown in (d) and (e). Mapping of elements Ni and P are shown in (b) and (c), respectively. Morphology of corresponding position is shown in the SEM photograph (a).

Fig. 1(a) is the nickel deposit according to the nickel mapping in Fig. 1(b) and the line profile in Fig. 1(d). This indicates that the alloy powder is well covered by the nickel film. The concentration of nickel in the outside coating layer is higher than that within the powder. This is reasonable since the outside coating is a Ni–P alloy and contains over 95 wt.% nickel, while the alloy powder contains only 37 wt.% nickel. The layer of nickel deposit contains little phosphorous as Fig. 1(c) shows. The phosphorous content determined by ICP was about 4 wt.% in the nickel deposit layer. The deposit mass constitutes about 25 wt.% of the coated powder.

The change in XRD pattern for the $\text{Ti}_{0.35}\text{Zr}_{0.65}\text{Ni}_{1.2}\text{V}_{0.6}\text{Mn}_{0.2}$ alloy after chemical coating with Ni–P and Ni, respectively, is shown in Fig. 2. The main difference between

bare powder and the Ni–P coated powder is the appearance of nickel phosphate (-220), (-323) and nickel (111). The Ni–P deposit has a crystalline structure. The difference between bare alloy powder and the powder coated with Ni is the appearance of nickel peaks. The Ni–P deposits may produce the Ni_3P structure under heat treatment [15,16], but this did not appear to happen in Ni–P coated electrodes after curing at 250°C for 20 min, as shown in Fig. 3. It is probable that the temperature and time for the curing were not sufficiently high and long to produce the Ni_3P structure. The structures of nickel phosphate (-220), (-323) for Ni–P coated electrodes disappear after 60 charge/discharge cycles. This is because nickel phosphate tends to dissolve in aqueous KOH during cycling. The amount of dissolved nickel phos-

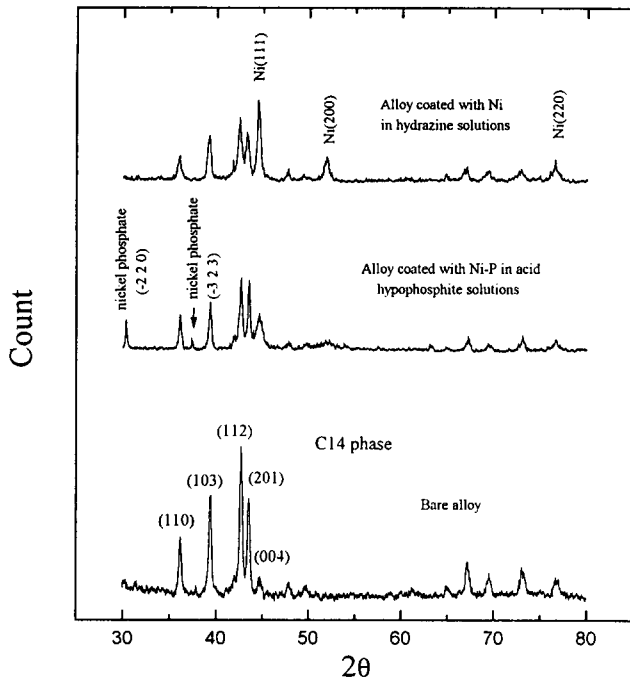


Fig. 2. Change in XRD pattern for $\text{Ti}_{0.35}\text{Zr}_{0.65}\text{Ni}_{1.2}\text{V}_{0.6}\text{Mn}_{0.2}$ alloy after chemical coating by Ni-P and Ni, respectively.

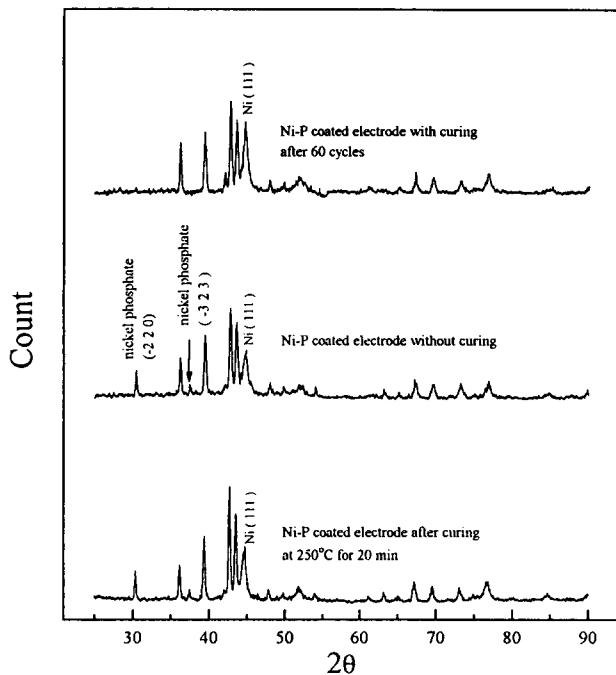


Fig. 3. XRD pattern of Ni-P coated electrodes under various curing conditions.

phate is too small to have any influence on the electrochemical performance of the electrodes.

3.2. Activation and cycle-life behaviour

The effect of cycling on the discharge capacity of electrodes after deposition with Ni-P or Ni was examined at a constant discharge current of 25 mA g (Fig. 4). Electrodes

A and B require about 10 cycles to reach their maximum discharge capacity (activation). By contrast, electrode C needs almost 40 cycles to reach its maximum capacity.

The activation behaviour is closely related to an increase in active surface area of the electrode in contact with the electrolyte. Several components of the alloy (i.e., Ti, Zr and V) easily form passive oxides that greatly inhibit the dissociation of water molecules and the absorption of hydrogen atoms. On the other hand, the oxides of V and Mn are both soluble in alkaline solution as HV_2O_5^- and manganese ion, respectively. This makes the electrode surface more porous. During cycling, the expansion and contraction of lattices associated with the absorption and desorption of hydrogen cause the bare alloy powder to crack. These cracks provide fresh surfaces to promote the hydrogen electrode reaction. Nickel powder has been found [17] to be a good compacting material for activation. Accordingly, an electrode mixed with nickel powder (electrode A) needs about the same number of cycles as the Ni-P coated electrode (electrode B) for activation.

Although the alloy within Ni-P coating can be kept fresh and is free of oxidation, electrode B still requires cycling (about 10 times) to produce sufficient active surface by repeated cracking. The cracking rate for producing the active surface area plays an important role in activation. Therefore, electrodes containing nickel powder and electrodes with Ni-P coating require nearly the same number of cycles for activation. The dissolving ability of the metal oxides in contact with alkaline electrolyte is an important factor for the cracking rate. Based on BET data, Fetceko et al. [18] found that the change in surface area of the metal hydride electrode is very high after cycling. They concluded that cracking can be regarded as creating a new surface area that plays an

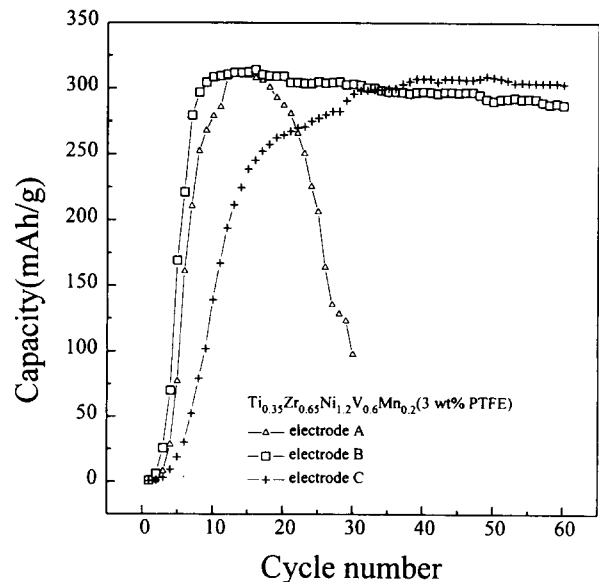


Fig. 4. Effect of cycling on discharge capacity of nickel powder mixed, Ni-P coated and Ni-coated alloy electrode, respectively. Electrode A: nickel powder mixed alloy electrode; electrode B: Ni-P coated alloy electrode, and electrode C: Ni-coated alloy electrode.

Table 3
Concentration of alloy components except for Ni dissolved in plating baths after coated ^a

Bath type	Ti (ppm)	Zr (ppm)	V (ppm)	Mn (ppm)
A ^b	32.58	43.67	310.17	172.17
B ^c	0.514	1.510	1.200	2.670

^a Alloy weight/bath volume = 1 g/50 cm³.

^b A: nickel electroless plating baths with hypophosphite as a reducer.

^c B: nickel electroless plating baths with hydrazine as a reducer.

important role in the discharge kinetics. Naito et al. [19] also found that appreciable disintegration of Ni–P coated alloy particles occurred after cycling.

The reason why electrode C requires about 40 cycles to reach its maximum capacity is that the oxide layer between the Ni layer and the fresh alloy interferes with the cracking process. Because the coating layer of the metal oxides prohibits the metal oxides from coming into direct contact with the alkaline electrolyte, the alloy within the dense oxides is insulated from cracking. The crack of the Ni-coated electrode (electrode C) is induced only by the expansion and contraction of the lattice. Thus, the electrode requires many more cycles for activation than electrode A or electrode B.

When preparing the alloy powder, the activation in H₂ gas at 400 °C may leave some oxides unremoved, and the fresh powder after activation may become oxidized when in contact with the alkaline plating baths at 83 °C. The reason why the oxides can be preserved in a hydrazine bath (powder for electrode C) rather than in an acid hypophosphite bath (powder for electrode B) is that the metal oxides are much more soluble in acid solutions containing fluorine ion, and are relatively stable in alkaline baths during the short plating period in comparison with a prolonged cycling process. Therefore, electrode C contains oxides and requires longer cycling than electrode B. In the case of electrode A, however, the oxides did dissolve in alkaline electrolyte during charge and discharge. This is why electrode A has a very short activation period. This difference is confirmed by the amount of the alloy components dissolved in the bath after plating, as shown in Table 3.

The maximum discharge capacities of the three types of electrodes are nearly the same, probably because both nickel powder and nickel coating act as microcurrent collectors and can equally improve electric conductivity. Iwakura et al. [20] observed that the maximum capacity decreased by mixing with metal oxides with low electric conductivity and increased by mixing with more conductive metal oxides.

Surface modification of the alloy by chemical nickel plating is indeed effective in improving the electrode's ability to maintain discharge capacity, as illustrated in Fig. 4. The discharge capacity of electrode A decays sharply after reaching maximum capacity. This may be ascribed to the continuous oxidation of fine powder during cycling. The mixed nickel powder is unable to protect the fresh hydride from oxidation,

but the nickel coating can act as an oxygen barrier and prevent the fresh alloy surface from oxidation. Nevertheless, the coated film is gradually damaged owing to the expansion and contraction of the lattice after repeated cycling. Accordingly, the discharge capacity slowly decreases.

3.3. High-rate dischargeability and chargeability

The current density dependence on the discharge capacity for the three types of electrodes is given in Fig. 5. There is a slight difference in the discharge capacity between electrode A and electrode B if the discharge current density is below 100 mA/g. In this study, we define the high-rate dischargeability as the discharge capacity at discharge current between 200 and 300 mA/g. Fig. 5 shows that the discharge capacity of electrode mixed with nickel powder (electrode A) at 300 mA/g was 62.5 mAh/g after 12 cycles. In the case of electrode B, the discharge capacity at 300 mA/g increased to 140 mAh/g. By contrast, the Ni-coated electrode (electrode C), gave a larger discharge capacity (viz., 200 mAh/g) at 300 mA/g after 40 cycles than that after 30 cycles (160 mAh/g). This means that the nickel coatings do indeed improve the high-rate dischargeability when compared with electrode A. In addition, the Ni-coated alloy electrode (electrode C) exhibits a better performance in high-rate dischargeability than the Ni–P coated alloy electrode.

Sakei et al. [7] found that high-rate dischargeability of LaNi_{4.7}Al_{0.3} alloy was greatly improved by copper coating due to the role of copper as a microcurrent collector in facilitating the charge-transfer reaction on the alloy surface. Iwakura et al. [20] observed that the high-rate dischargeability decreased by mixing with metal oxides with low electric conductivity and increased by mixing with more conductive

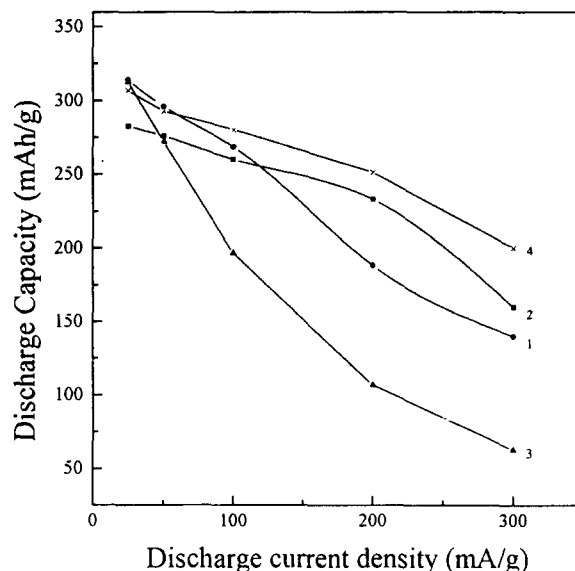


Fig. 5. Discharge capacity as a function of discharge current density for modified electrodes discharged at 30 °C: (1) electrode B, 20 cycles; (2) electrode C, 30 cycles; (3) electrode A, 12 cycles, and (4) electrode C, 40 cycles.

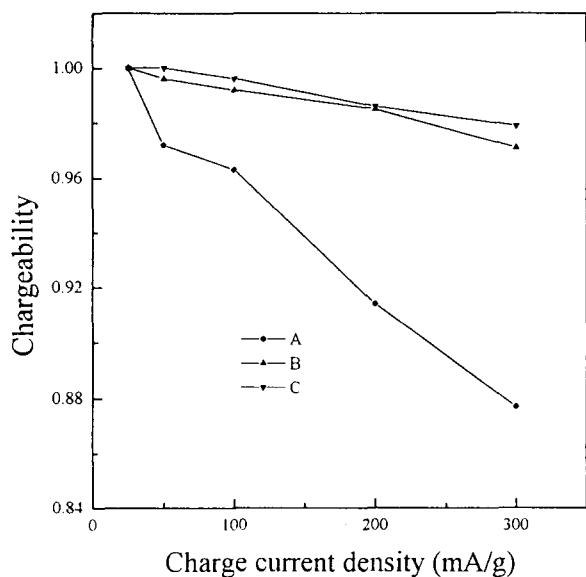


Fig. 6. Dependence of chargeability of A, B and C electrodes on charge current density: (A) electrode A, 12 cycles; (B) electrode B, 20 cycles, and (C) electrode C, 40 cycles.

metal oxides. Accordingly, the electric conductivity of metal coating or compacting material has great influence on the high-rate dischargeability of metal hydride electrode. Naito et al. [19] found that the content of phosphorus in Ni–P deposit affects greatly the electric conductivity of the deposit. The Ni–P coating with 10 wt.% P is characterized by a high electric resistance ($67 \mu\Omega \text{ cm}$) compared with that ($119 \mu\Omega \text{ cm}$) of the Ni–P coating with 3.5 wt.% P. Hence, the increment in phosphorous content may decrease the electric conductivity of the deposit. A pure Ni coating should have better electric conductivity than a Ni–P coating. The superior behaviour of the Ni-coated alloy electrode compared with the Ni–P coated alloy electrode in high-rate dischargeability may be attributed to its better electric conductivity.

The chargeability of the three types of electrodes was examined by charging each with the same amount of electricity at various current densities (25, 50, 100, 200, and 300 mA/g) followed by discharge at 25 mA/g (Fig. 6). The charge capacity was controlled at 1.3 times the discharge capacity. The chargeability can be defined as a ratio of C_x to C_{25} , where C_x indicates the discharge capacity at 25 mA/g discharge current and x mA/g charge current, and C_{25} indicates the discharge capacity at 25 mA/g discharge current and 25 mA/g charge current. Thus, C_x/C_{25} physically means the coulombic efficiency at various charge rates relative to C_{25} . Fig. 6 shows the fractional difference of chargeability between the two types of nickel-coated electrode. This difference is rather limited in the charge current range of 25 to 100 mA/g for the nickel powder mixed electrode (electrode A) and the nickel-coated electrodes (electrodes B and C). This is because in the low current range, the alloy has superior hydrogen-absorbing ability and the plateau pressure is below 1 atm [4] and the effect of nickel coating to retard hydrogen release is not significant. The chargeability of the coated

alloy electrodes is significantly better, however, than that of the bare alloy electrodes if the charge current exceeds 100 mA/g. The chargeability at a high charge rate is therefore influenced by the ability to release hydrogen. The coated nickel film acts as a barrier for hydrogen release and provides sufficient time for hydrogen absorption into the alloys.

3.4. Resistance against capacity deterioration during overdischarge

Sakai et al. [9] found that the surface modification of electrodes by Cu or Ni–P coating is very effective in preventing the inner pressure rise of sealed cells during overcharge and overdischarge. This means that micro-encapsulation of the alloy powder can improve the safety during overcharge and overdischarge. The potential capacity loss due to overdischarge was not discussed. The ability to preserve capacity is a very important index for industrial applications. Because metal hydride undergoes an anodic reaction during discharge, serious oxidation can cause great damage to the discharge capacity. To avoid excessive oxidation, the cutoff voltage was usually set at around -0.6 V (versus Hg/HgO). This ability to preserve capacity was examined by discharging at 25 mA/g to $+0.4 \text{ V}$ (versus Hg/HgO) and then leaving the electrodes at open-circuit for 15 h. The recovery efficiency of the discharge capacity to the initial state was measured by six cycles of charge and discharge, as illustrated in Fig. 7. The recovery efficiency of the discharge capacity is an indicator of the retention of discharge capacity after overdischarge to $+0.4 \text{ V}$ (versus Hg/HgO) and is defined as the ratio of the discharge capacity after overdischarge to that of the initial state. The recovery efficiency of electrode B after overdischarge is much higher than that of electrode A. Without the protection of a continuous

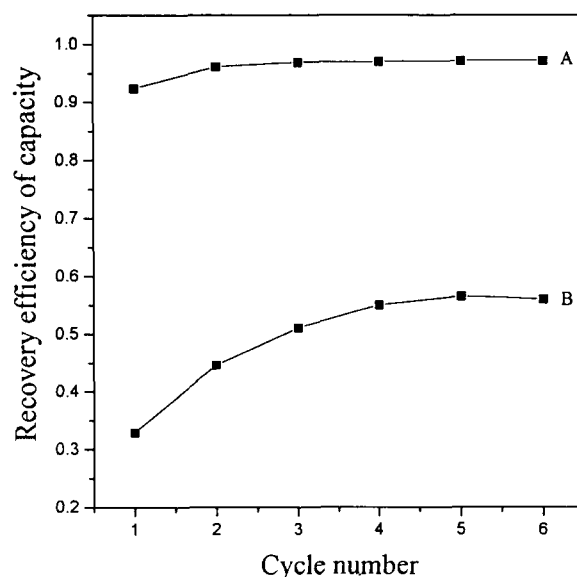


Fig. 7. Recovery efficiency of discharge capacity to initial state after overdischarging to 0.4 V (vs. Hg/HgO): (A) Ni–P coated alloy electrode, and (B) nickel powder mixed alloy electrode.

nickel alloy coating, electrode A loses its capacity very quickly after overdischarge. The Ni–P coated alloy electrode retains over 90% of its initial capacity after overdischarge. This indicates that a Ni–P coated layer provides excellent protection against oxidation of the active alloy in Ni/metal hydride batteries.

3.5. Electrochemical performance of duplex nickel-coated alloy electrodes

As described above, electrode B requires far fewer activation cycles than electrode C. On the other hand, electrode C provides better high-rate dischargeability in comparison with electrode B. It is very interesting to combine the two coating steps together on the alloy powder. The purpose is to develop an electrode that possesses the merits of both electrode B and electrode C. Hence, a process of duplex nickel plating was developed. In this, the alloy was first coated with Ni–P and then coated with Ni. The weight ratio of the Ni–P coating to the Ni coating was 2:3. The total nickel deposit mass was 30 wt.% of the coated powder.

An investigation was also made of the factors that control the high-rate dischargeability of the modified electrodes. The dischargeability is controlled by two processes: one a kinetic process, the other a diffusion process. With increase in discharge current density, one of the two processes becomes more important than the other and, thereby, determines the rate capability of the overall electrode reaction. If the diffusion of hydrogen atoms (or OH^-) through the coated film is the dominating process, then the high-rate discharge capacity of the duplex nickel-coated electrode will be determined by the slower diffusion step between the Ni–P and Ni-coated films. If the charge-transfer process dominates, then the high-rate discharge behaviour will be influenced heavily by the electric conductivity of the alloy surface [7]. For the duplex nickel-coated electrode, the kinetic process dominates the overall electrode reaction at high rates (Fig. 8). This is reflected by the fact that the high-rate dischargeability of the duplex nickel-coated electrode is similar to that of the Ni-coated alloy electrode, cf., Fig. 8 with curve 4, Fig. 5. If the dischargeability of the Ni–P or the Ni-coated alloy electrode is controlled by the diffusion process, the high-rate discharge performance should be similar to that of the rate-determining layer of either the Ni–P or the Ni coating. Hence, the duplex nickel-coated electrode should perform similarly to electrode B which has a poorer high-rate dischargeability than electrode C. By contrast, the high-rate dischargeability of the duplex nickel-coated electrode is virtually the same as that of electrode C. For example, the discharge capacity (246 mAh/g) of the duplex nickel-coated electrode at 200 mA/g discharge current after 20 cycles is about equal to that (251 mAh/g) of electrode C after 40 cycles. Thus, the defect of a single Ni–P coating is avoided by this new nickel-coating method. Since the high-rate dischargeability of these modified electrodes (i.e., electrode B, electrode C, duplex nickel-coated alloy electrode) is dominated principally by the charge-trans-

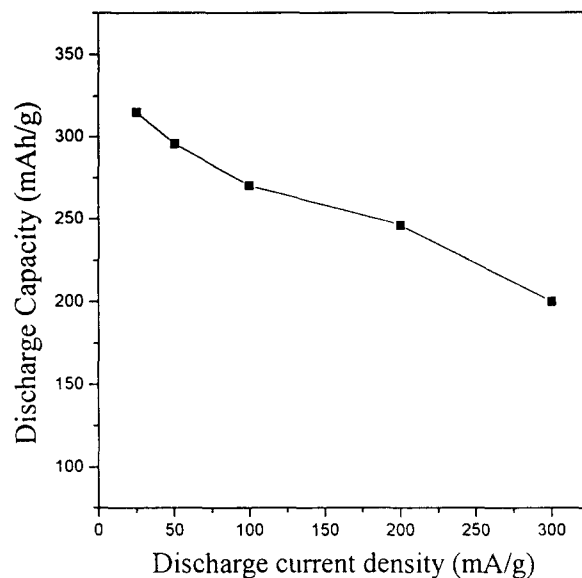


Fig. 8. Dependence of discharge capacity of duplex nickel-coated alloy electrode on discharge current density.

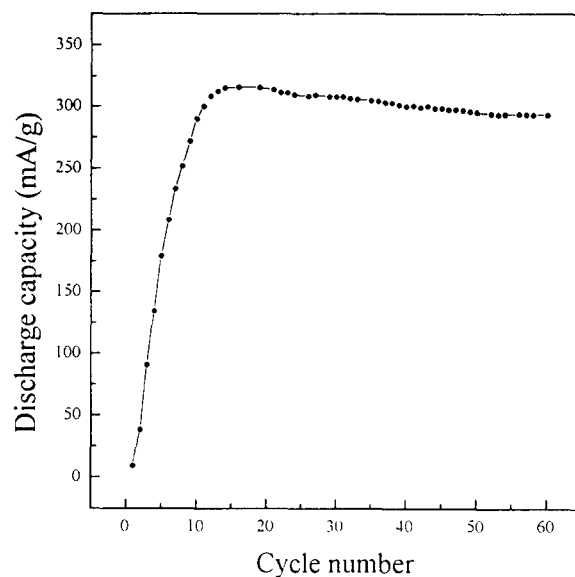


Fig. 9. Effect of cycling on discharge capacity of duplex nickel-coated alloy electrode.

fer process, as opposed to the diffusion process, the superficial layer on the coated alloy powder does not appear to hinder hydrogen permeation to any significant extent. Hence, the thickness of the various nickel deposits in this work is not an important determinant of high-rate dischargeability.

Surprisingly, it was also found that the activation behaviour of the duplex nickel-coated electrode is similar to that of electrode B, cf., Fig. 9 with curve B, Fig. 4. This is probably because when Ni–P film is first coated on the alloy, the metal oxides are removed and the Ni–P film protects the active surface of the alloy. In addition, the resistance of the duplex nickel-coated electrode against capacity deterioration during overdischarge is as good as that of Ni–P coated alloy electrode, cf., Fig. 10 and curve A, Fig. 9. For example, the

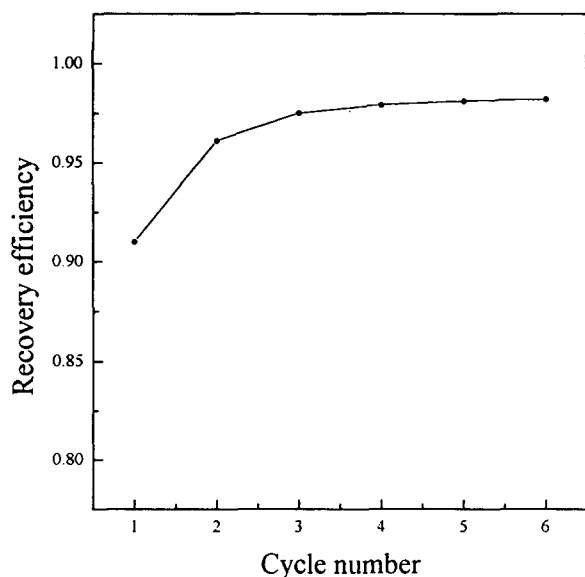


Fig. 10. Recovery efficiency of discharge capacity to initial state for duplex nickel-coated alloy electrode after overdischarge.

recovery efficiency of the duplex nickel-coated electrode is over 0.9 at the first cycle after overdischarge. The duplex nickel coating therefore imparts both better high-rate dischargeability and fast activation behaviour. The duplex nickel-coating method proposed in this study should be a promising method for surface modification of metal hydride electrodes.

4. Conclusions

1. Electrodes modified by either Ni–P or Ni coatings display improvements in high-rate dischargeability and discharge stability. The high-rate dischargeability of the Ni-coated alloy electrode is superior to that of the Ni–P coated alloy electrode. The activation cycles required for the Ni-coated electrode, however are four times as long as those for the electrode coated with Ni–P.

2. Oxidation of the hydrogen storage alloy affects adversely high-rate dischargeability, activation behaviour, and

cycle life. A nickel-coated layer provides excellent protection against oxidation of the hydride electrode.

3. A duplex nickel coating that contains both Ni–P and Ni films performs satisfactorily with respect to both high-rate dischargeability and activation behaviour.

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