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Effects of AB_5-type hydrogen storage alloy prepared by different techniques on the properties of MH/Ni batteries

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Abstract

The effects of hydrogen storage alloy prepared by different preparation techniques with composition $Mm(NiCoMnAl)_5$ on the properties of MH/Ni batteries have been investigated. Compared with as-cast alloy, as-quenched and as-quenched+annealed alloy could produce advantages to the battery in high rate dischargeability, internal pressure, cycle lifetime and internal resistance at beginning of cycles. Unfortunately, the rapidly quenched alloy slowed down the initial activation rate of the battery voltage, but after annealing, the rate would improve slightly. The influence of the alloy from different preparation techniques on the capacity and voltage of batteries is slight. The annealing would mainly improve the high rate dischargeability and depress the internal pressure contrasted with the as-quenched alloy. The differences can be ascribed to the change of phase and microstructure caused by different preparation techniques.

Keywords: Hydrogen storage alloy; Cast; Quench; Anneal; The properties of batteries

1. Introduction

The MH/Ni batteries using hydrogen storage alloys as the negative material have been developed and have become the main competitor to Ni–Cd batteries due to higher power densities, low memory effects and more environmentally friendly constituents [1]. The AB_5-type hydrogen storage alloy is one ideal material for MH/Ni battery application nowadays since a remarkable improvement of electrochemical cycling durability was achieved by Willems and Buschow [2]. It has been found that the performance of the alloy depends on the alloy composition as well as the preparation conditions. In recent years, increasing cooling rate during solidification has been attracting research activity. Electrochemical properties of AB_5-type alloys prepared by different techniques, such as capacity, cycle lifetime, electrode potential and so on, have been largely measured by means of half-cells [3–7]. The results showed that compared with cast alloy, the durability of the quenched alloy can be greatly improved at the expense of a small decrease in capacity, and rapid quenching can also flatten the discharge voltage plateau, but the rapidly quenched alloy slowed down the initial activation rate. In addition, the influence of the anneal on the quenched alloy with composition $ML(NiCoMnTi)_5$ has been studied [8,9]. But the effects of hydrogen storage alloy from different techniques on the properties of MH/Ni batteries are rarely reported, such as the battery capacity, activation speed, cycle lifetime, high rate dischargeability, especially the battery internal pressure and resistance. In this study, the influence of hydrogen storage alloys prepared by different techniques on the properties of MH/Ni batteries is reported.

2. Experimental details

2.1. Preparation of the alloys

A base ingot of the $Mm(NiCoMnAl)_5$ alloy was prepared by induction melting and cooled in a copper mould which was cooled by water. All the raw materials had a purity of >99.9%. Part of the cast alloy was re-melted and rapidly quenched to flakes by melt-spinning with a single copper wheel under an argon atmosphere, and then parts of the rapidly quenched alloy were vacuum annealed for 1 h at 673 K. Three kinds of alloys with the same composition were pulverized mechanically to powder lower than 250-mesh.

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2.2. The electrode preparation

The test electrodes were prepared by paste-type technology and nickel foam served as the substrate. Hydrogen storage alloy powder and nickel powders were mixed thoroughly in a weight ratio of 100:5. A suitable amount of aqueous suspension containing carboxymethyl cellulose (CMC) and polytetrafluoroethylene (PTFE) dispersion solution as binders were added to the mixed powder and mixed again to obtain slurry. The slurry was pasted on to the nickel foam, and then dried in air for 45 min in an oven at 100°C, pressed and cut into a dimension of 105×40×0.4 mm.

The positive nickel electrodes were prepared by mixing sphere $Ni(OH)_2$ as active material, nickel and cobalt hydroxide powders as additives, loading in a porous nickel foam substrate using CMC and PTFE as binders. Then they were dried at 80°C in air for 1 h before pressing to a dimension of 75×40×0.7 mm.

2.3. The battery preparation

All experiments in this work were taken on an AA size cylindrical sealed-type Ni–MH battery in which both the positive electrode and negative electrode were mounted spirally through a separator, and the electrolyte was a 6 M KOH solution containing 1 M $LiOH \cdot H_2O$. In the test batteries, the positive nickel electrodes are the same; the negative metal hydride electrode is prepared by as-cast alloy, as-quenched alloy, and as-quenched+annealed alloy, respectively. Five batteries were made for each alloy to calculate the average value of the battery characteristics.

2.4. Measurements of the battery characteristic

Three kinds of batteries composed of as-cast, as-quenched and as-quenched+annealed alloy separately were activated by eight cycles at 0.1*C* rate charging for 15 h and 0.2*C* rate discharging down to 1.0 V (*C* corresponds to the current needed to discharge the total capacity of the positive electrode in 1 h). Afterwards, the capacity and voltage were tested according to the following conditions: charge at 0.5*C* for 2.5 h, discharge at the same rate down to 1.0 V. The high rate dischargeability was investigated by charging at 1*C* for 1.2 h, keeping for 30 min at open-circuit, and then discharging at 1*C*, 2*C* and 3*C* rate down to 0.9 V, separately.

The battery internal resistance was measured with a DK-3000 precision internal resistance instrument. The internal pressure test was carried out by opening a small hole of 1.5 mm in diameter in the battery cap, putting into a sealed container and shielding a pressure sensor through an O-ring. The test conditions were as follows: charge at 0.5*C* for 150 min, after a 20 min pause, discharge at 0.5*C* down to 1.0 V; charge at 1*C* for 80 min, after a 60 min pause, discharge at 1*C* down to 1.0 V. The internal pressure in the whole process of charge and discharge were recorded.

Constant-current charge–discharge cycles were performed at 25±1°C on a charge–discharge instrument controlled by a computer. The test batteries were charged at 1*C* for 1.2 h, kept for 30 min, and then discharged at 1*C* down to 0.9 V, and the cycle continued at intervals of 30 min.

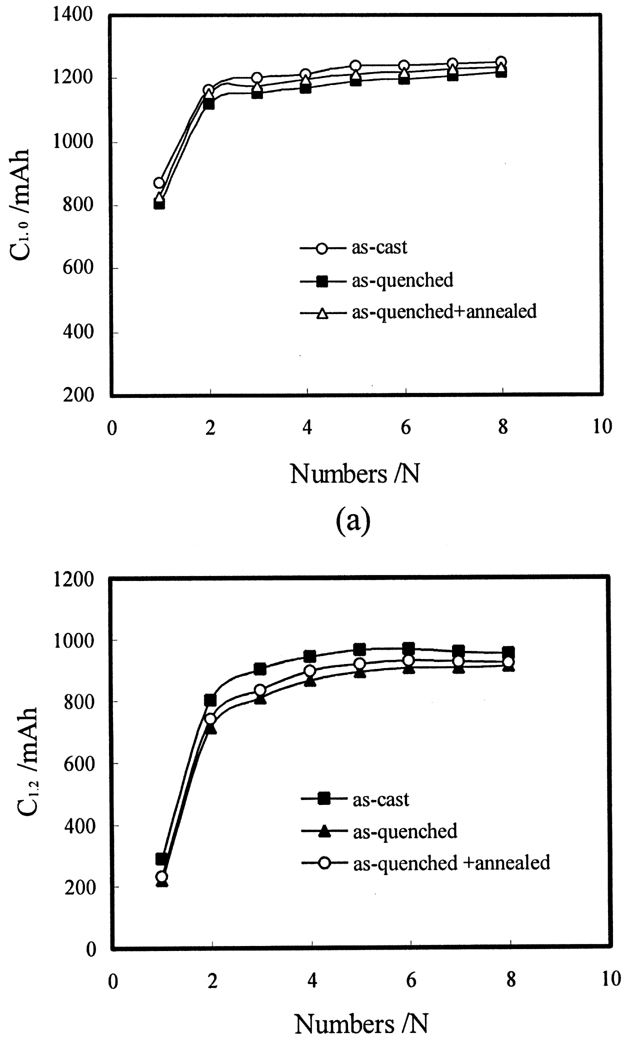
3. Results and discussion

3.1. The activation characteristics of the batteries

According to Li [7,10], it is more difficult to activate completely the as-quenched alloy than the as-cast one with the same composition $Mm(NiCoMnAl)_5$, and the initial activation of the alloy is very sensitive to the solidification rate. The typical capacity and voltage characteristic of the batteries during the first eight cycles are shown in Fig. 1. $C_{1.2}$ and $C_{1.0}$ represents the capacity of the batteries discharged down to 1.2 V and 1.0 V, separately. $C_{1.2}$ could describe the battery voltage characteristic. The larger the value of $C_{1.2}$, the better the voltage characteristic. The results show that the activation rate of capacity is nearly the same because the capacity is positive limited, but there is some difference in the activation rate of voltage. The rapidly quenched alloy slowed down the initial activation rate of the battery voltage, but after annealing, the rate would improve slightly. This phenomenon resulted from the decrease in capacity of the negative electrode alloy. After eight cycles, the voltage characteristic could be close to that of a battery employing as-cast alloy as negative electrode material. So it needs more cycles to activate the batteries composed of as-quenched or as-quenched+annealed alloy so that the batteries are fully activated.

3.2. The capacity and the voltage of the batteries

The average capacity and the voltage were measured at 0.5*C* rate after activation. The stable capacity after 10 times charge/discharge cycle was taken as the real capacity of the batteries. As shown in Table 1, the capacity and voltage of the batteries in which as-cast alloy was employed as negative electrode material is excellent, rapid quenching leads to a decrease and lower voltage characteristic. The annealing technique could improve the capacity, but has no apparent benefit on the voltage. The results are in agreement with the electrochemical measurement made on the alloy powder by means of a half-cell. But taking one with another, the influence of the alloy from different preparation techniques on the capacity and voltage of batteries is slight, and the metal hydride negative electrode prepared by these techniques totally satisfies the practice application in respect of capacity and voltage.



(a)

(b)

Fig. 1. The activation curves of capacity (a) and voltage (b) of the battery comprised of different negative electrode alloys.

3.3. The internal pressure characteristics of the batteries

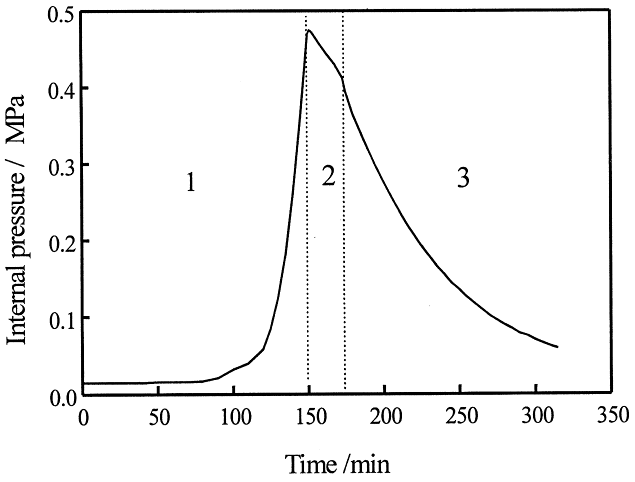


Fig. 2. The typical internal pressure curve of the AA-type MH/Ni battery during (1) charging; (2) open-circuit; (3) discharging.

Fig. 2 shows a typical change of internal pressure behavior in the charging and discharging process of the sealed-type MH/Ni battery. In section 1, the internal pressure climbs up excessively at the end of charge. Section 2 is the interval, the pressure goes on slightly increasing up to the maximum value (P_{max}) and then begins to climb down slowly. Section 3 represents the process of discharging, the internal pressure decreased rapidly. When the voltage is 1 V or 0.9 V, the internal pressure drops to the minimum value (P_e). Therefore, the recombination ability of the battery is characterized by the recombination percentage (R) according to the following formula:

Table 1
The capacity and voltage of the batteries in which the alloys prepared by different techniques were used as negative electrode material

Alloy	As-cast	As-quenched	As-quenched + annealed
$C_{1.2\ V}$ (average value)	867	861	861
$C_{1.0\ V}$ (average value)	1191	1150	1166

$$R = \frac{P_{max} - P_e}{P_{max}} \times 100\%.$$

The sufficient recombination percentage is beneficial to the cycle lifetime; otherwise, the internal pressure could be accumulated to the higher value even if it is lower at the beginning.

Fig. 3 represents the internal pressure comparison of the battery in which the negative electrode was prepared by as-cast, as-quenched, as-quenched + annealed alloy separately. It shows that the internal pressure performance is strongly dependent on the preparation condition of the alloy. Whether charging/discharging at 0.5C or 1C rate, the rapid quenching alloy can decrease internal pressure in comparison with casting, and the anneal technique could bring about a lower pressure.

It is well known that the overall electrochemical reactions, occurring at both electrodes during charging (ch) and discharging (d) can, in their most simplified form, be represented by:

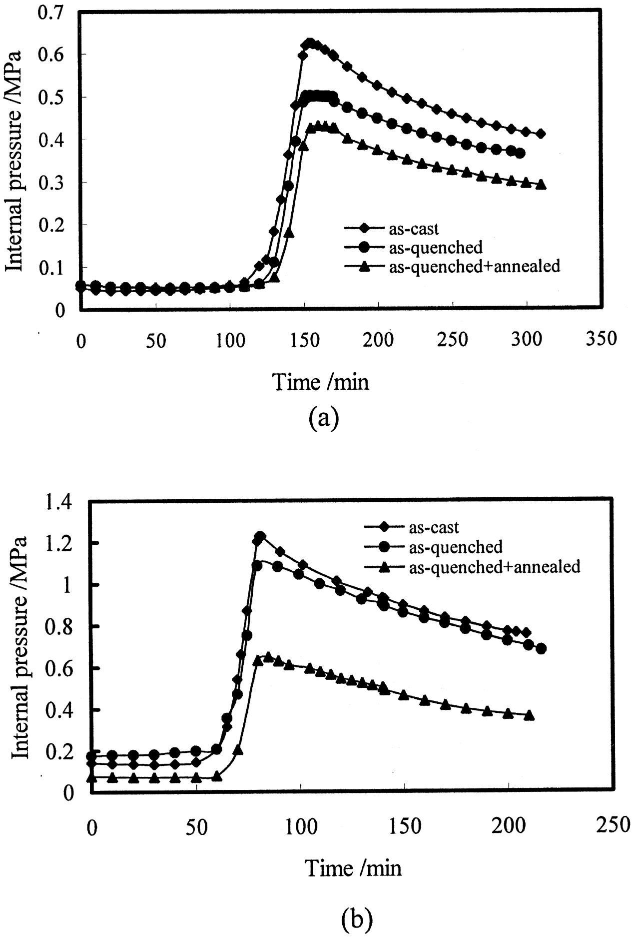
positive

$$\mathrm{Ni(OH)_2} \underset{d}{\overset{ch}{\rightleftarrows}} \mathrm{NiOOH} + \mathrm{H}^+ + \mathrm{e}^- \tag{1}$$

$$\mathrm{H}^+ + \mathrm{OH}^- \underset{d}{\overset{ch}{\rightleftarrows}} \mathrm{H_2O} \tag{2}$$

negative

$$\mathrm{H_2O} + \mathrm{e}^- \underset{d}{\overset{ch}{\rightleftarrows}} \mathrm{H_{(ad)}} + \mathrm{OH}^- \tag{3}$$



(a)

(b)

Fig. 3. The internal pressure curves of the batteries charged/discharged at (a) 0.5*C*; (b) 1*C* rate.

$$MH_{(x-1)} + H_{(ad)} \underset{d}{\overset{ch}{\rightleftarrows}} MH_{x(ads)} \tag{4}$$

During charging, divalent Ni^{2+} is oxidized into the trivalent Ni^{3+} state and water is reduced to hydrogen atoms (H_{ad}) which are first sized at the surface of the hydrogen storage alloy and then absorbed into the alloy ($MH_{x(ads)}$). The reverse reaction takes place during discharging. The net effect of this reaction sequence is that hydroxyl ions in the electrolyte are transported from one electrode to the other and hence that no electrolyte consumption takes place during current flow. But usually the positive electrode is the capacity-determining electrode, as a result, a side-reaction that is oxygen evolution occurs at the positive nickel electrode during overcharging according to:

$$4OH^- \xrightarrow{ch} O_2 + 2H_2O + 4e^- \tag{5}$$

Then, the sealed battery becomes a complicated system composed of solid, liquid, gas phase, each reaction taking place at a different interface. The partial oxygen pressure starts to rise due to oxygen evolution, advantageously, oxygen can pass through the separator and diffuses onto the negative electrode where it can be reduced at the MH/electrolyte interface in hydroxyl ions at the expense of reaction (3):

$$O_2 + 2H_2O + 4e^- \underset{d}{\overset{ch}{\rightleftarrows}} 4OH^- \tag{6}$$

Assuming that this recombination reaction is functioning properly, the partial oxygen pressure can be lower. According to the battery design, the battery internal pressure is derived from the partial oxygen pressure without consideration of overdischarging.

But in practical usage, especially at rapid charging, there is also a side-reaction (Tafel reaction) in the negative electrode during charging:

$$H_{ad} \rightarrow \frac{1}{2}H_2 \tag{7}$$

If the diffusion of adsorbed atomic hydrogen to the bulk of hydrogen storage alloy (Eq. (4)) is not sufficiently faster than the adsorbed atomic hydrogen formation reaction, hydrogen is generated (Eq. (7)). When some oxide film exists at the surface of the negative electrode, or the hydrogen plateau pressure is inclined, or the alloy capacity is lower, these factors could make the reaction (4) slower and the reaction (7) faster. Ref. [11] showed that the hydrogen evolution could take place more or less during charging accompanied by oxygen evolution, the ratio of the oxygen/hydrogen depends on the charging current.

In this paper, quenching and anneal technique made the alloy form a different phase and microstructure, X-ray diffraction patterns and SEM observations indicated [7] that the master alloy is more inhomogeneous in composition and has more atomic disorder. Segregation is found in the as-cast alloy, while there is none in the as-quenched alloy whose crystal grain is much smaller than that of the as-cast alloy. Single phase and homogeneous structure can flatten the voltage plateau, this would benefit the reaction (4), so the hydrogen evolution coming from the negative electrode can be suppressed. Owing to the same positive nickel electrode, the oxygen evolution is the constant in test batteries, accordingly, the less the partial hydrogen pressure, the lower the internal pressure of the battery. Compared with the as-quenched alloy, a much flatter discharge plateau can be obtained at appropriate annealing temperature, because annealing caused the growth of grains, the removal of defects in the crystals and disorder of the atoms rather than production of a new phase. Therefore, the battery composed of as-quenched+annealed negative electrode alloy has the lowest internal pressure.

As seen in Table 2, the recombination percentage of these batteries is very close to one another. It indicated that the lower pressure and the larger recombination percentage

Table 2
The internal pressure of the batteries in which the alloys prepared by different techniques were used as negative electrode material

Charge/discharge rate	The internal pressure	As-cast	As-quenched	As-quenched + annealed
0.5*C*	P_{max} (MPa)	0.624	0.501	0.431
	P_e (MPa)	0.410	0.364	0.290
	R (%)	34	27	33
1*C*	P_{max} (MPa)	1.229	1.086	0.651
	P_e (MPa)	0.756	0.68	0.362
	R (%)	38	37	44

could improve the cycle durability with the exception of the as-cast alloy.

3.4. The high rate discharge characteristics of the batteries

It is well known that the discharge capacity of the batteries decreased with increasing the discharge rate. The rapid dischargeability can be defined as

$$\text{High rate dischargeability } (C_h) = (C_x/C_{0.5}) \times 100\%$$

where C_x and $C_{0.5}$ are the discharge capacity of the battery discharging at x rate ($x = 1C$, $2C$, $3C$) and $0.5C$ rate, respectively. Table 3 gives the high rate dischargeability of the investigated batteries composed of as-cast, as-quenched and as-quenched + annealed alloy. From Table 3, it can be found that rapid quenching or annealing is helpful to enhance the capacity discharging at high rate, the high rate dischargeability of the as-cast alloy is smaller than that of as-quenched and as-quenched + annealed alloy. As pointed out previously [12], the low value of high rate dischargeability was ascribed to the overvoltage induced by charge-transfer resistance and by hydrogen diffusion delay. Apparently, rapid quenching and annealing could advance the hydrogen diffusion in the negative electrode alloy.

3.5. The cycle lifetime of the batteries

Fig. 4 shows the typical discharge capacity of the investigated batteries as a function of cycle number. After 300 cycles, the capacity decay rate of the battery composed of as-cast alloy was larger than as-quenched and as-quenched + annealed alloy, and the best cycle durability can be obtained by annealing technique.

Table 3
The high rate dischargeability of the batteries in which the alloys prepared by different techniques were used as negative electrode material

Alloy	The high rate dischargeability at different discharge rates (%)		
	1*C*	2*C*	3*C*
As-cast	97.9	95.1	88.2
As-quenched	99.2	98.5	95.7
As-quenched + annealed	98.6	97.8	94.3

In Ref. [13], the relation between the microstructure and the cycle lifetime of the alloy was studied. The author pointed out that there was much segregation in the inner part of the as-cast alloy and the grain size was very large, which could cause the alloy to pulverize and to oxidize faster. But in as-quenched and as-quenched + annealed alloy annealed at appropriate temperature, there was no segregation and the grain size was very small, which decreased the pulverization of the alloy particle. Moreover, an amorphous phase in the as-quenched alloy could depress the surface oxidation of the alloy.

In fact, the cycle lifetime of the battery depends on not only the positive and negative electrode material performance but also many other factors, such as electrolyte, separator and so on. The cycle lifetime represents the comprehensive characteristics of the battery. At present, we found that the long cycle lifetime is mainly ascribed to the lower internal pressure. Sometimes the negative electrode itself has not decayed but the higher internal pressure made the alkaline electrolyte leak and decrease in electrolyte volume, then the cycle lifetime deteriorates. So the results of charge/discharge cycle are in agreement with the change of internal pressure mentioned before.

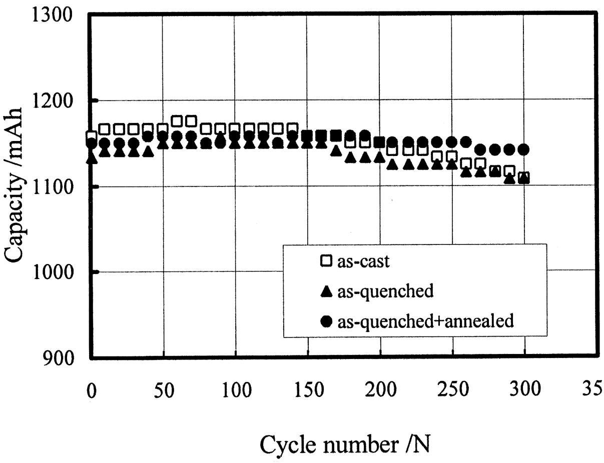


Fig. 4. The cycle lifetime characteristics of the battery comprised of different negative electrode alloys charged/discharged at 1*C* rate.

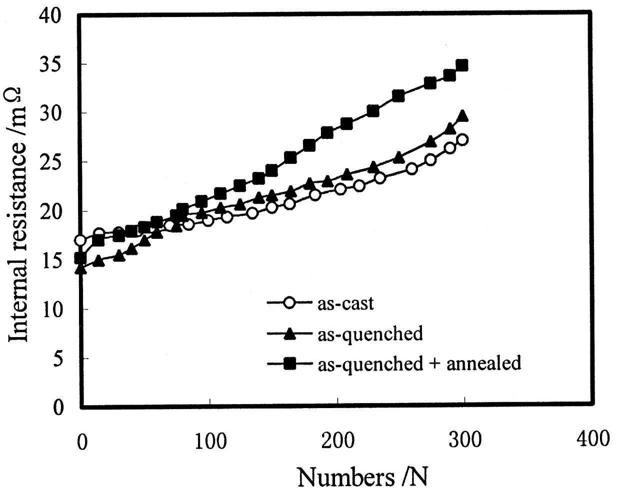


Fig. 5. The internal resistance of the battery comprised of different negative electrode alloys as a function of cycle numbers.

3.6. The internal resistance of the batteries

Generally speaking, the internal resistance would increase with the charge/discharge cycle. In Fig. 5, at the beginning of cycles, the average internal resistance of the battery composed of as-quenched or as-quenched+annealed alloy is smaller. But they increase faster and exceed the battery composed of as-cast alloy nearly 100 cycles later. The phenomenon is possibly related to the grain size of the negative electrode alloy, and it requires further study and elucidation.

4. Conclusions

The effects of hydrogen storage alloy from different preparation techniques with composition Mm(NiCoMnAl)$_5$ on the properties of the batteries have been investigated. Compared with as-cast alloy, as-quenched and as-quenched+annealed alloy could produce advantages to the battery in high rate dischargeability, internal pressure, cycle lifetime and internal resistance at beginning of cycles at the expense of a slight decrease in activation rate and the capacity as well as voltage characteristics of the battery. The annealing would mainly improve the high rate dischargeability and depress the internal pressure contrasted with the as-quenched alloy. The differences can be ascribed to the change of phase and microstructure resulting from different preparation techniques.

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