ELECTRODE CHARACTERISTICS OF NANOCRYSTALLINE $LaNi_5$ PREPARED BY MECHANICAL ALLOYING①

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ABSTRACT The potential application of nanocrystalline $LaNi_5$ as rechargeable battery negative electrode material was investigated. Nanocrystalline $LaNi_5$ was synthesized by ball milling a mixture of La and Ni elemental powders. The TEM morphology of this nanocrystalline $LaNi_5$ powder showed that it had an average grain size of 50 nm. It was found that electrode prepared with nanocrystalline $LaNi_5$ had a comparable discharge capacity, in comparison with the negative electrode prepared with polycrystalline coarse grained $LaNi_5$, and had easier activation behavior and longer cycling lifetime. These novel properties were attributed to the special structure of nanocrystalline $LaNi_5$ caused by mechanical alloying.

Key words nanocrystalline nickel-metal hydride battery mechanical alloying electrode characteristics

1 INTRODUCTION

As a new type of rechargeable battery, the nickel-metal hydride batteries using hydrogen storage alloys as negative electrode materials have attracted much attention over recent years. This new type of battery exhibits a higher energy density and has no memory effect, as compared with conventional Ni-Cd battery. In addition, it uses no Cd or other toxic heavy metals[1, 2]. At present, AB_5 system hydrogen storage alloys are mainly used in Ni/MH batteries. Rapid decay of discharge capacity by repetition of charge and discharge is a remaining problem for these misch-metal-based multicomponent hydrogen storage alloys. It is regarded that the decrease of discharge capacity is caused by selective oxidation of misch-metal on the electrode surface and continual disintegration of alloy powder during repeated cycling[3].

Nanocrystalline materials are polycrystalline materials with grain size of up to 100 nm. Because of the extremely small dimensions, a large volume fraction of the atoms is located at the grain boundaries. It was reported that the properties of nanocrystalline materials are very often superior to those of conventional polycrystalline coarse grained materials[4]. With very fine grain size, nanocrystalline hydrogen storage materials are expected to be hardly pulverized by repetition of charge and discharge when they are used as negative electrode materials for Ni/MH batteries. Therefore the cycle lifetime of metal hydride electrode might be improved by using nanocrystalline hydrogen materials as negative electrode materials. In this study, nanocrystalline $LaNi_5$ was synthesized by mechanical alloying. The electrochemical properties of this nanocrystalline powder were measured and compared with those of coarse grained $LaNi_5$.

2 EXPERIMENTAL

The synthesis of nanocrystalline $LaNi_5$ was accomplished by ball milling stoichiometeric mixture of elemental powder (purity > 99%) in a

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planetary mill using hardened steel balls and vial with a ball-to-powder ratio of 40∶1, milling speed of 400 r/min, protection of argon atmosphere. The coarse grained $LaNi_5$ was prepared from 99% pure metals by arc melting in argon atmosphere. The homogeneous alloy was obtained by turning out and remelting the alloy four times. The alloy was crushed and mechanically ground to particle size without annealing.

The $LaNi_5$ electrode was prepared by pasting an alloy slurry onto two sides of a piece of Ni foam plate with a size of 20 mm × 20 mm. The alloy slurry consisted of a dispersed mixture of alloy powder and binder emulsion (3% PVA solution). After being dried, the electrode was pressed under 6 MPa. The test cell consisted of one $LaNi_5$ electrode, two $Ni(OH)_2$ electrodes which sandwich the $LaNi_5$ electrode and a separator for separating the two kind of electrodes. The total capacity of the two $Ni(OH)_2$ electrodes was much larger than that of the $LaNi_5$ electrode. The cell was sandwiched between two pieces of organic glass in order to compact the electrodes. For measuring discharge capacity, the cell was immersed in a beaker which was filled with 6 mol/L KOH solution. The charge-discharge cycles were carried out on a charge-discharge controller at room temperature (293 K). The electrode was charged at $50\,mA\cdot g^{-1}$ for 8 h and discharged at $50\,mA\cdot g^{-1}$ after 5 min resting time. The end discharging was set to − 0.9 V.

Phase analysis and micro-morphology of the nanocrystalline $LaNi_5$ and coarse grained $LaNi_5$ were performed by X-ray diffractometer (XRD) and TEM.

3 RESULTS AND DISCUSSION

3.1 Alloy formation

In order to monitor the alloy formation, a small amount of the ball milled powder was intermittently taken out from the ball mill after every milling hour. These small quantities of powder was subjected to XRD characterization. Fig. 1 gives XRD patterns of the mixture powder of La-5Ni milled for various periods. Fig. 1(a) is the representative XRD pattern of the mixture La-5Ni before milling which as expected shows separate element peaks corresponding to La and Ni. The XRD pattern of the sample ball milled for 2 h (Fig. 1(b)) shows that the peaks corresponding to La almost disappeared, and those corresponding to Ni slightly decreased in intensity without other obvious change. Fig. 1(c) presents an intermediate stage of mechanical alloying reaction (after ball milling for 5 h). It shows that along with $LaNi_5$ some free Ni was also present, and the peaks corresponding to Ni decreased in intensity and got broadened. Finally the XRD pattern for a sample ball milled for 10 h reveals the clear and prominent peaks of $LaNi_5$. The final diffraction pattern exhibits a broadening of the peaks characteristics for nanocrystalline materials.

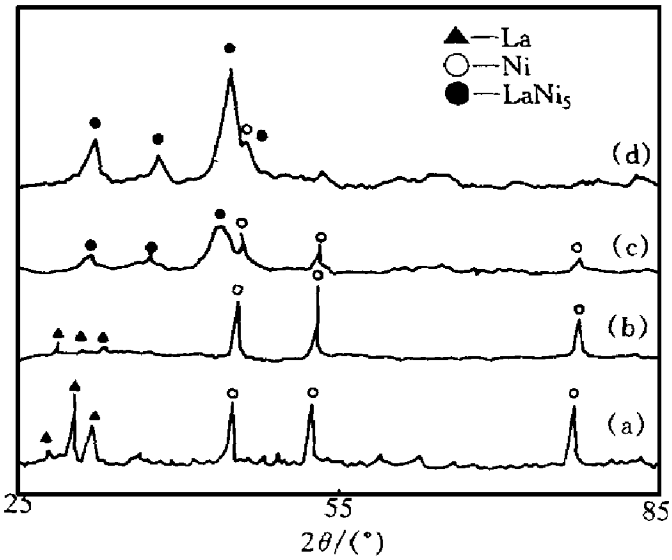

Fig. 1 XRD patterns for La-5Ni powder as a function of milling time
(a) —0 h; (b) —2 h; (c) —5 h; (d) —10 h

Fig. 2 shows the transmission electron morphology of mechanically alloyed $LaNi_5$. It was found that the average size of the particles of the compound was about 3 μm (Fig. 2(a)), while the average grain size in particles was about 50 nm (Fig. 2(b)).

3.2 Electrode activation

Fig. 3 shows the discharge capacities of the electrodes at the first four cycles. It was found that the electrode prepared with coarse grained

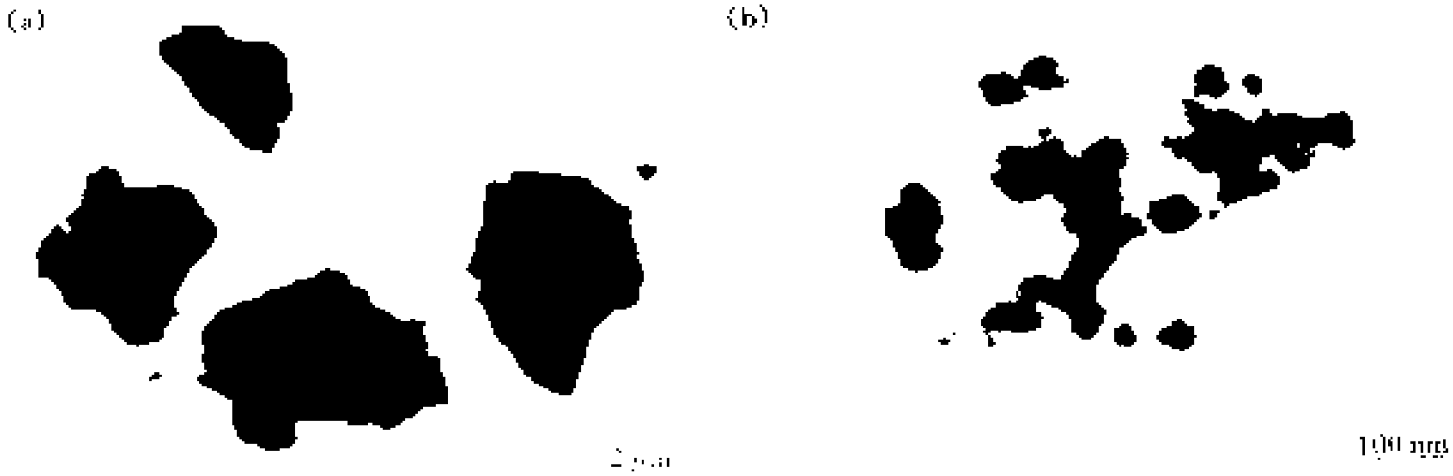

Fig. 2 TEM morphologies of La-5Ni powder ball milled for 10 h
(a) —× 8 000; (b) —× 80 000

$LaNi_5$ showed a smaller initial discharge capacity (Fig. 3(a)). The electrode prepared with nanocrystalline $LaNi_5$ showed excellent activation behavior (Fig. 3(b)). It reached its highest discharge capacity at the fourth cycle.

Gleiter H *et al* regarded that nanocrystalline materials contain a very large fraction of atoms at the grain boundaries, the numerous interfaces provide a high density of short diffusion paths. Consequently they are expected to exhibit an enhanced diffusion in comparison with conventional coarse grained polycrystalline materials with same composition[5]. In ball milling process, frequent fragmentation and cold-welding produce a large quantities of active surfaces of alloy with high stress which make the surface electrochemical reaction easier[6]. In this study, nanocrystalline $LaNi_5$ was synthesized by mechanical alloying. It had higher density of short circuit diffusion paths and much fresher active interfaces in comparison with coarse grained $LaNi_5$. This led to a result that the nanocrystalline $LaNi_5$ electrode had a much easier activation behavior than the coarse grained $LaNi_5$ electrode.

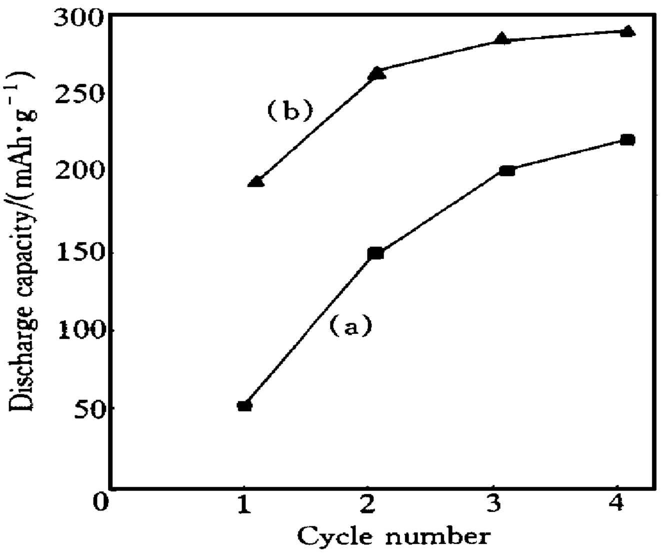

Fig. 3 Discharge capacities of electrode prepared with coarse grained $LaNi_5$(a) and nanocrystalline $LaNi_5$(b) at first four cycles

3.3 Durability of electrodes

Fig. 4 shows the discharge capacities of the electrodes as a function of charge-discharge cycling number. It was found that the discharge capacity of the electrodes prepared with nanocrystalline $LaNi_5$ decreased about 10% in the first twenty cycles and decreased more slowly in following cycles. On the contrary, the discharge capacity of the electrode prepared with coarse grained $LaNi_5$ decreased a little in the first 100 cycles, but decreased rapidly in following cycles. After 140 cycles, the electrode prepared with nanocrystalline $LaNi_5$ had a higher discharge capacity than electrode prepared with coarse grained $LaNi_5$. The difference became

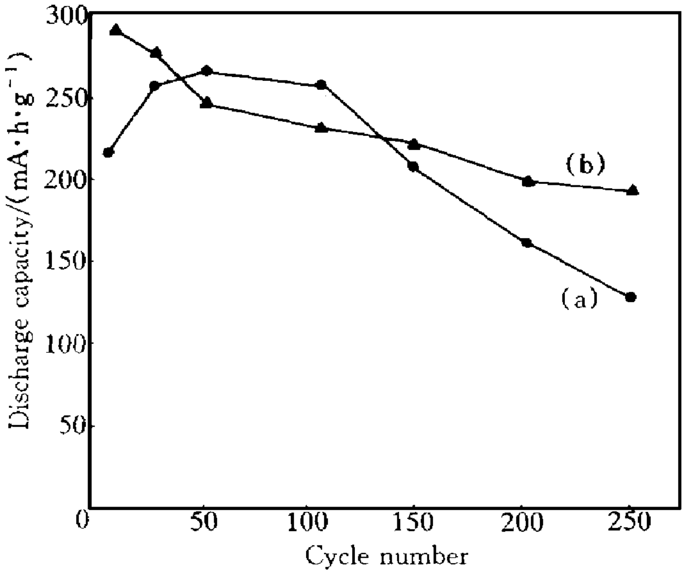

Fig. 4 Discharge capacities of alloys prepared with coarse grained $LaNi_5$(a) and nanocrystalline $LaNi_5$(b) as a function of cycle number

larger and larger as the cycles number increased.

Schlapbach *et al* clarified that $LaNi_5$ has a surface layer composed of Ni cluster embedded in $La(OH)_3$. Since the hydride $LaNi_5H_6$ is easily oxidized to $La(OH)_3$ and Ni by directly contacted with KOH solution, the surface oxide layer is considered to work as a protective barrier to oxidation[6]. Sakai *et al* observed that the charge-discharge cycles pulverized the AB_5-compounds finally below 5 μm[7]. In our study, the nanocrystalline $LaNi_5$ have an average particle size of about 3 μm and an average grain size of 50 nm. Since the numerous fresh surfaces were easily oxidized. So the discharge capacity of the electrode prepared with nanocrystalline $LaNi_5$ decrease a lot in the first 10 cycles. Because the crystal size was very fine, the grains didn't decrepitate during charge discharge cycles. The particle size was so small that the particles might not be pulverized. This resulted that the discharge capacity of the electrode prepared with nanocrystalline $LaNi_5$ deceased very slowly in the following cycles. On the contrary, the coarse grained $LaNi_5$ had an average grain size of about 10 μm and the grains in particles were coherent. At the beginning of cycles, the stress in particles increased gradually and the particles didn't cracked heavily, so that the discharge capacity of the electrode prepared with coarse grained $LaNi_5$ decrease little. As the cycle number increased, the stress located in qarticles increased to a maximum volume and the particles began to crack heavily. So the discharge capacity of the electrode prepared with coarse grained $LaNi_5$ decreased very rapidly from then on.

Fig. 5 presents the XRD patterns of the powders removed from the electrodes cycled for 250 times. Fig. 5(a) shows that the peaks corresponding to $La(OH)_3$ and Ni are stronger than those corresponding to $LaNi_5$ which exhibit broadening of the peaks characteristic for nanocrystalline material. This indicates that the coarse grained $LaNi_5$ had been pulverized into nanocrystalline and heavily oxidized. On the contrary, the oxidation of nanocrystalline $LaNi_5$ electrode was much slighter, which is shown in Fig. 5(b).

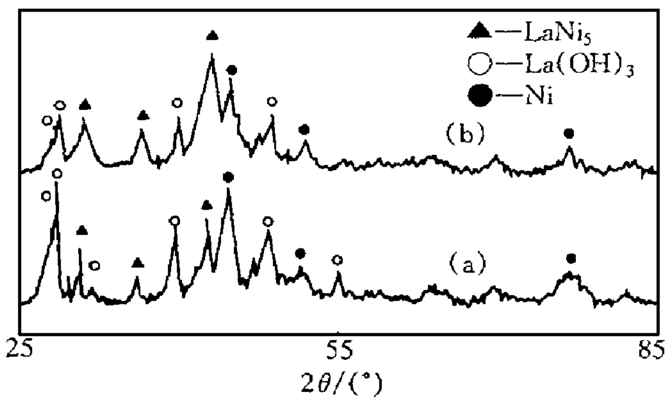

Fig. 5 XRD patterns of powders removed from electrodes prepared with coarse grained $LaNi_5$(a) nanocrystalline $LaNi_5$(b) after 250 charge-discharge cycles

According to above results, the longer cycle lifetime of the $LaNi_5$ electrode, which was expected by using nanocrystalline $LaNi_5$ as negative electrode materials for Ni/MH battery, was achieved. This finding suggests that the promising application for nanocrystalline hydrogen materials as negative electrode for Ni/MH battery.

4 CONCLUSIONS

Nanocrystalline $LaNi_5$ with an average size of about 50 nm was synthesized by mechanical alloying. In comparison with the electrode prepared with conventional coarse grained $LaNi_5$, the electrode prepared with this nanocrystalline powder had a comparable discharge capacity, much easier activation behavior and longer cycle lifetime. These excellent properties were ascribed to the fresh active interfaces, the high surface-to-volume ratio and fine particle size of nanocrystalline $LaNi_5$.

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