

The effects of pulse charging on inner pressure and cycling characteristics of sealed Ni/MH batteries

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Abstract

The effects of pulse charging technique on inner pressure and cycling characteristics of sealed Ni/MH batteries were investigated by comparison with the conventional direct current (DC) charging. The electrochemical impedance spectroscopy of cycled Ni/MH batteries have been measured. The micrographs of individual electrodes in the batteries have also been examined by SEM. Experimental results show that pulse charging is an effective approach to lower the internal pressure of battery during charge and overcharge, moreover, the appropriate frequency is $t_p = 5$ s and $t_n = 1$ s in our experiments. The battery charged by pulse current exhibits slower capacity fade rate and smaller overpotential at the same charge–discharge rate. In addition, the anode charged by pulse current exhibits less serious pulverization than that charged by DC charging. The possible explanation is that the short relaxation periods interspersed during the charging process can effectively eliminate the concentration polarization and increase the power transfer rate, thus accelerating the charging process, reducing the gas evolution reaction, slowing down the pulverization rate of electroactive materials and keeping the water absorption capability of separator constant.

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1. Introduction

Due to its high energy density, high rate capability, long cycle life and better environmental compatibility, Ni/MH batteries have conquered important shares of rechargeable battery market and exhibiting more and more extensive applications [1–4]. As a kind of sealed rechargeable battery, the basic principle of the design is the realization of the so-called “oxygen cycle” during the stage of overcharge by the “positive-electrode-limited” capacity. However, the evolution of gas consequentially gives rise to the change of inner pressure of battery. An increase in cell pressure above a certain value, i.e., about 20 atm, causes a release of gas from the safety valve in normally sealed cells, leading to unwanted drying of the electrolyte solution and a decrease of the cycle life due to an increased ohmic loss. Thus the inner pressure is an important parameter for Ni/MH batteries.

To reduce the inner pressure of the Ni/MH battery during charge and overcharge, many works have been carried

out. Sakai et al. [5] reported the effect of alloy powder coated with Cu or Ni and alloy powder mixed with Cu or Ni on the inner pressure of batteries. Moreover, when alloys coated with porous copper [6] were used in sealed Ni/MH batteries, longer cycle life and a higher discharge capability were achieved. Lee and co-workers [7] reported that the Zr–Ti–Mn–V–Ni alloy electrode was fabricated by mixing the alloy with Cu powder. By replacing 50% of carbon black with Cu powder, the inner cell pressure rarely increased with cycles. Additionally, Lee and co-workers [8] also reported that the Zr-based hydrogen storage alloy electrode was fabricated by mixing the alloy with Ni powder with high surface area. By replacing 25% of carbon black with filamentary Ni powder, the inner cell pressure can be suppressed significantly. Mao et al. [9] reported that the effect of three kinds of cobalt powder with different mean diameter added to the negative electrode on the inner pressure of Ni/MH batteries during charging was examined. Experiments showed that batteries with finer Co powder displayed a much lower inner gas pressure on charging than batteries with coarser Co powder. Wu and co-workers [10] used ring-metalated porphyrin doped on the hydrogen storage alloy electrode of Ni/MH battery as electrochemical catalyzer

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to accelerate the oxygen gas consumption reaction and lower the inner pressure of battery. Anyhow, we notice that the intention for all above-mentioned methods is to improve the surface catalytic activity of the hydrogen storage alloy electrode and quicken the oxygen gas consumption reaction in sealed Ni/MH battery.

Actually, besides to quicken the oxygen gas consumption rate by improving the surface catalytic activity of the anode in sealed Ni/MH battery, we can also adopt some methods to lower the oxygen gas evolution rate. Kohl and co-workers [11] studied the effects of a pulse charging technique on charge–discharge behavior and cycling characteristics of commercial lithium-ion batteries. The results showed that the pulse charging is helpful in eliminating concentration polarization, increasing the power transfer rate, and lowering charge time by removing the need for constant voltage charging in the conventional protocol. Nelson et al. [12] adopted pulse charging to inhibit the sulfation of the negative plate and increase cycle life of lead-acid battery. However, the effects of pulse charging on inner pressure and cycling characteristics of commercial Ni/MH batteries have not been reported.

In this paper, the inner pressure and cycling characteristics of Ni/MH batteries charged by the pulse charging were compared with that by a traditional direct current (DC) charging method. Meanwhile, the microstructure of the electrodes in the batteries after cycling under two kinds of charging protocols were also studied using scanning electron microscopy (SEM).

2. Experimental

A typical waveform of pulse current during charge and overcharge is shown in Fig. 1. This waveform is determined by three independent parameters: i_p , t_p and t_n , where i_p is the pulse peak current, t_p the “on” time span of a pulse and t_n the “off” time span of a pulse. The pulse period is the sum of t_p and t_n . Thus the average current during charge is expressed by the following equation:

$$i_m = \frac{t_p}{t_p + t_n} i_p \quad (1)$$

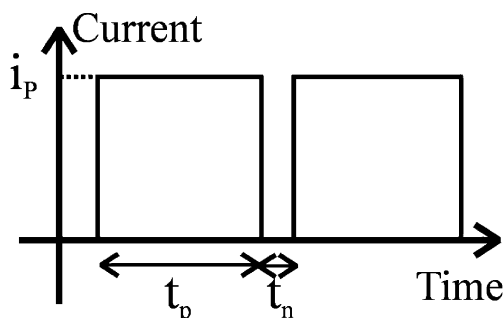


Fig. 1. A typical waveform of pulse current during charge and overcharge.

The commercial Ni/MH batteries used in this study came from JJJTM (Guangdong, China) AA-type cells with nominal capacity of 1200 mAh. These batteries were subjected to a few 0.1–0.2 C charge–discharge cycles to verify their normal capacities and behavior before employed in experimental studies. The experimental set-ups employed in these works are schematically shown in [13,14]. The batteries charged by pulse current were cycled under the following scheme: the battery was charged at the average current of 1 C ($t_p = 5$ s and $t_n = 1$ s) for 72 min, and then discharged at the constant current of 1 C down to 1.0 V. The batteries charged by DC charging were cycled according to the following scheme: the battery was charged at a direct current of 1 C for 72 min, and then discharged at the constant current of 1 C down to 1.0 V. After the batteries were cycled for 200 times, the electrochemical impedance measurements of batteries with 20% SOC were carried out on an EG & G PARC model 273 impedance spectroscopy system coupled with M398 software. The positive terminal of the battery was used as the working electrode. The negative terminal of the battery was used as the counter electrode and the reference electrode. The voltage perturbation used in the present work was ± 5 mV. Impedance was measured from 10^{-3} to 10^3 Hz.

Following the impedance measurements, the discharged batteries were carefully disassembled. The cathodes and anodes were immediately placed into distilled water for 5 h to remove the KOH adsorbed on the electrodes. The treated electrodes were dried and then prepared for microscopy examination. The surface morphologies were observed by means of a scanning electron microscopy (ISI-SX-40).

3. Results and discussion

3.1. The effects of pulse charging on the inner pressure of Ni/MH batteries

Fig. 2 shows the typical profile of changes of internal pressure with time when a Ni/MH cell was charged and overcharged for 40 min at the average current of 2 C with different pulse frequency, then the cell was discharged at the constant current of 400 mA down to 1.0 V. The internal pressure remains negligible during the initial period of charging, but it starts to increase rapidly when the charging process is almost completed. The inner pressure during charge and overcharge increases with the decreasing frequency of pulse charge. It can be seen that the inner cell pressure for direct current charge attains 27 atm at the end of the charge and overcharge process, whereas the inner cell pressure for pulse charge ($t_p = 5$ s and $t_n = 1$ s) only attains 13 atm, about a half of the former. Moreover, we can find that the lower the pulse charge frequency is, the earlier the inner pressure goes up. As for the pressure fluctuation on Curve 3 in Fig. 2, it comes from the low frequency of pulse charge current. In detail, during charge and overcharge process, when a Ni/MH cell is charged at the current of 2.9 A for 5 min, the inner

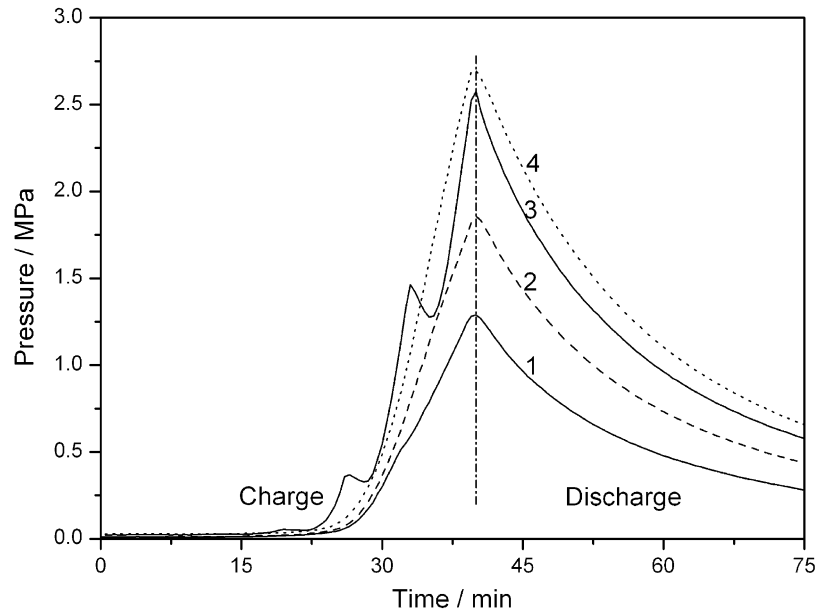


Fig. 2. The profile of changes of internal pressure with time when a Ni/MH cell was charged for 40 min at the average current of 2C with different pulse frequency, then the cell was discharged at the constant current of 400 mA down to 1.0 V: (1) $t_p = 5$ s and $t_n = 1$ s, (2) $t_p = 20$ s and $t_n = 4$ s, (3) $t_p = 5$ min and $t_n = 1$ min, (4) DC charge.

cell pressure more rapidly ascended than that charged at a constant current of 2.4 A. During the rest of battery, because there is no gas evolution in this period, on the contrary, the inside oxygen gas can be consumed by the reduction reaction with the anode of battery, the internal pressure promptly decays. With the increase of pulse frequency, the pressure fluctuation is equalized, and so there is no obvious fluctuation on Curves 1 and 2 in Fig. 2.

By comparison with the changes of internal pressure of battery charged by different frequencies, we can know that

the pulse ($t_p = 5$ s and $t_n = 1$ s) is the best frequency to lower internal pressure in our experimental results. Fig. 3 shows that changes of internal pressure with time when a Ni/MH cell was charged at constant and pulse 1 C current for 80 min, and then discharged at the constant current of 400 mA down to 1.0 V. From this figure, we can observe that the experimental results are similar to those shown in Fig. 2. In detail, the inner cell pressure for direct current charge attains about 15 atm at the end of the charge and overcharge process, whereas the inner cell pressure for pulse charge (t_p

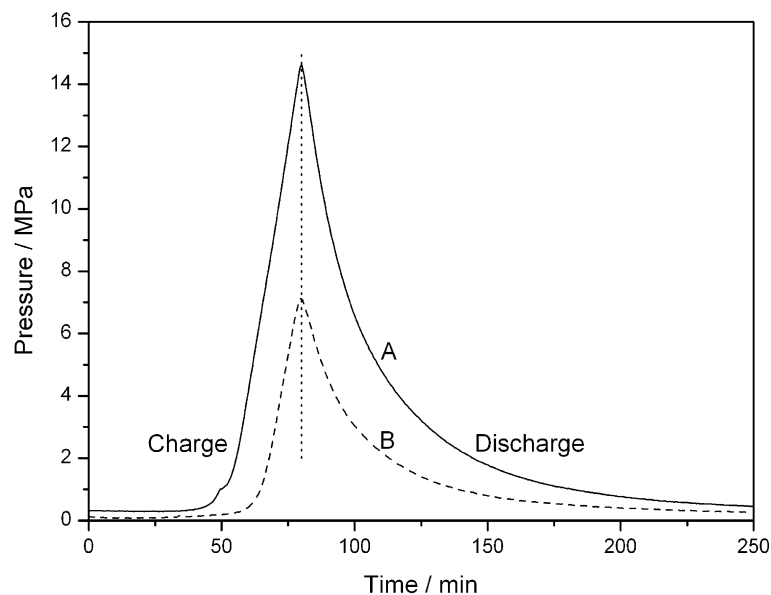


Fig. 3. The changes of internal pressure with time when a Ni/MH cell was charged at constant and pulse 1 C current for 80 min, and then discharged at the constant current of 400 mA down to 1.0 V: (A) DC charging and (B) pulse charging ($t_p = 5$ s and $t_n = 1$ s).

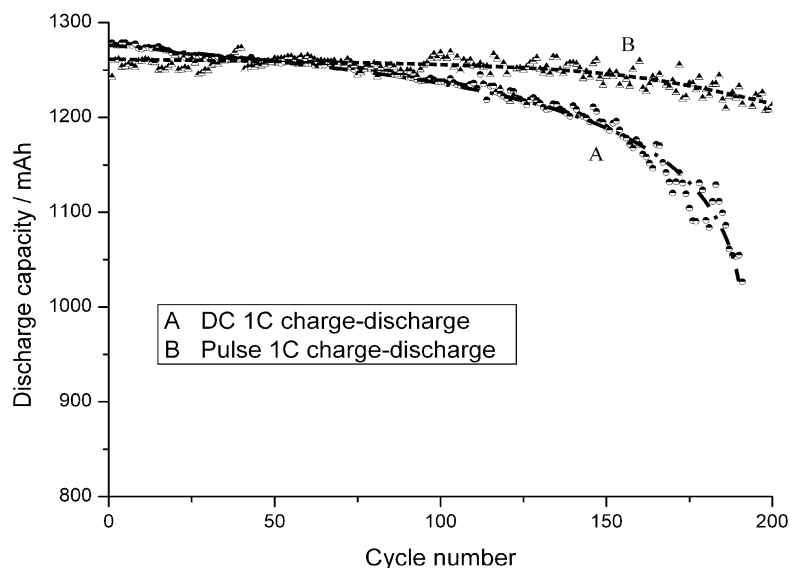


Fig. 4. Cycling performance of Ni/MH batteries using different charging scheme: (A) DC charge at 1 C for 72 min and then discharged at the constant current of 1 C down to 1.0 V, (B) pulse charge at 1 C ($t_p = 5$ s and $t_n = 1$ s) for 72 min and then discharged at the constant current of 1 C down to 1.0 V.

= 5 s and $t_n = 1$ s) only attains about 7 atm, also about a half of the former. Meanwhile we can find that the inner pressure of battery charged by DC charging goes up earlier than that charged by pulse current. All above experimental results show that the pulse charging is an effective approach to lower the internal pressure of battery during charge and overcharge, moreover, the appropriate frequency is $t_p = 5$ s and $t_n = 1$ s in our experiments. The possible explanation is that the short relaxation periods interspersed during the charging process can effectively eliminate the concentration polarization and increase the power transfer rate, thus accelerating the charging process and reducing the gas evolution reaction. Thus we employ the pulse frequency ($t_p = 5$ s and $t_n = 1$ s) to investigate the effects of pulse charging on cycling characteristics of Ni/MH batteries in this paper.

3.2. The effects of pulse charging on the cycling characteristics of Ni/MH batteries

The discharge capacities of the Ni/MH batteries charged by constant and pulse current as a function of the cycle number are shown in Fig. 4. All of the initial discharge capacities of the Ni/MH batteries are higher than the nominal capacity of the batteries (1200 mAh). From this figure, we can find that for the battery charged by direct current, the initial discharge capacity is 1275 mAh, and the discharge capacity at the 200th cycle is 1027 mAh, which decreased to 80% of the initial discharge capacity. However, for the battery charged by pulse charging, the initial discharge capacity is 1262 mAh, and the discharge capacity at the 200th cycle is 1212 mAh, which only decreased to 96% of the initial discharge capacity. Therefore, compared with the discharge capacity of the battery charged by DC

charge at the 1 C charge–discharge rate, the battery charged by pulse charge shows slower capacity fade rate at the same charge–discharge rate, although its initial discharge capacity is lower about 13 mAh than the former.

3.3. The effects of pulse charging on electrochemical impedance spectroscopy

After the batteries were cycled for 200 times, the electrochemical impedance measurements were carried out. The Nyquist plot of Ni/MH batteries charged by DC and pulse charging is shown in Fig. 5, which is mainly comprised of a semicircle at high frequency and a straight line at low frequency. The semicircle reflects the impedance of the electrochemical reaction of the battery, while the straight line indicates diffusion of the electroactive species. Solution

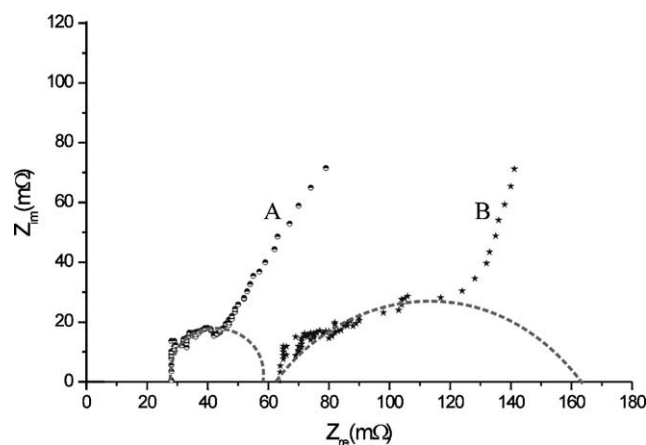


Fig. 5. Impedance spectroscopy of the Ni/MH batteries charged by DC and pulse 1 C charge–discharge after 200 cycles: (A) pulse charging ($t_p = 5$ s and $t_n = 1$ s), (B) DC charging.

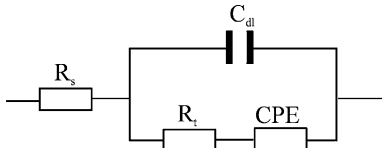


Fig. 6. Equivalent circuit for Ni/MH battery, where R_s is the total ohmic resistance of the solution and the separator as well as the electrodes, R_t is the charge-transfer resistance of the battery, CPE is the constant-phase element and C_{dl} is the double layer capacitor.

resistance is determined by the point of intersection of the semicircle with the real axis, including the total ohmic resistance of the solution, the separator and the electrodes. The model for the essential features of battery is represented by the electrical equivalent circuit [15–18] shown in Fig. 6.

The data were fitted using the equivalent circuit shown in Fig. 6. It is found that after the batteries were cycled for 200 times, the ohmic resistance R_s of battery charged by pulse charging is markedly smaller than that charged by DC charging. Likewise, the charge-transfer resistance of battery charged by pulse current is also markedly smaller than that charged by DC current. The possible reasons for the increase of the ohmic resistance and charge-transfer resistance during charge and discharge usually come from the following facts [4]: (1) dissolution (corrosion) of the hydrogen storage alloy (or some constituents of the alloy) in alkaline electrolyte results in the formation of oxides and hydroxides, such as $\text{La}(\text{OH})_3$, $\text{Al}(\text{OH})_3$ and LiMnO_2 , which gives rise to the water consumption in battery and the increase of charge-transfer resistance of the negative electrode. (2) Irreversible electro-oxidation of the separator results in the decrease of water absorption capability and the increase of separator resistance. (3) Gas evolution and con-

sumption reactions inside battery result in the accumulation of heat. High temperature makes separator decompose easily. (4) Expansion of electroactive materials oppresses separator and makes it lose water. From the internal pressure experiments, we know the battery charged by pulse current exhibits lower gas evolution and consumption rate than the battery charged by DC current, thus the battery by pulse charging possesses lower internal pressure and temperature during charge and overcharge. From the experimental results on electrochemical impedance spectroscopy, we can conclude that pulse charging can keep the water absorption capability of separator constant and slow down the growth of the ohmic resistance and charge-transfer resistance during cycling.

3.4. The effects of pulse charging on electrode microstructure

The cycled batteries were carefully disassembled and microstructures of the individual electrodes were examined using SEM technique. The surface morphologies of the cathodes are shown in Fig. 7. It can be seen that the active material still stays compact after 200 cycles. Moreover, there is not distinct difference on the microstructure of cathode charged by DC and pulse current. Nevertheless, the distinction on the anode micrographs in terms of grain size and grain distribution is obvious. In Fig. 8(A), particles are bulky and the size of some grains reaches $6\ \mu\text{m} \times 6\ \mu\text{m}$. In Fig. 8(B), particles with small size increase obviously, roughly $1\ \mu\text{m} \times 1\ \mu\text{m}$. Namely, the microstructure of anode charged by DC current exhibits more serious pulverization than that charged by pulse current. Meantime we can observe that the surface of anode charged by DC current is oxidized more obviously than that charged by pulse current.

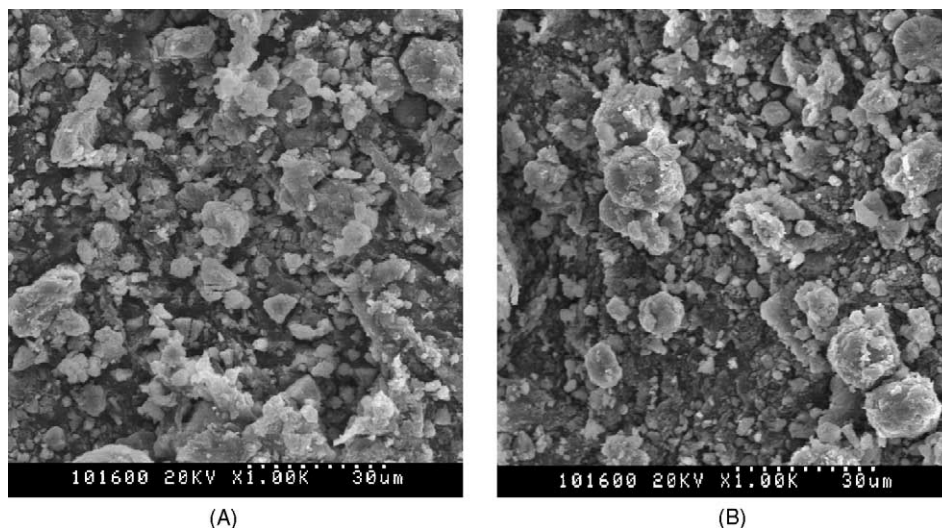


Fig. 7. Micrographs of cathodes of Ni/MH batteries charged by DC and pulse 1 C charge–discharge after 200 cycles: (A) pulse charge at 1 C ($t_p = 5\ \text{s}$ and $t_n = 1\ \text{s}$) for 72 min and then discharged at the constant current of 1 C down to 1.0 V, (B) DC charge at 1 C for 72 min and then discharged at the constant current of 1 C down to 1.0 V.

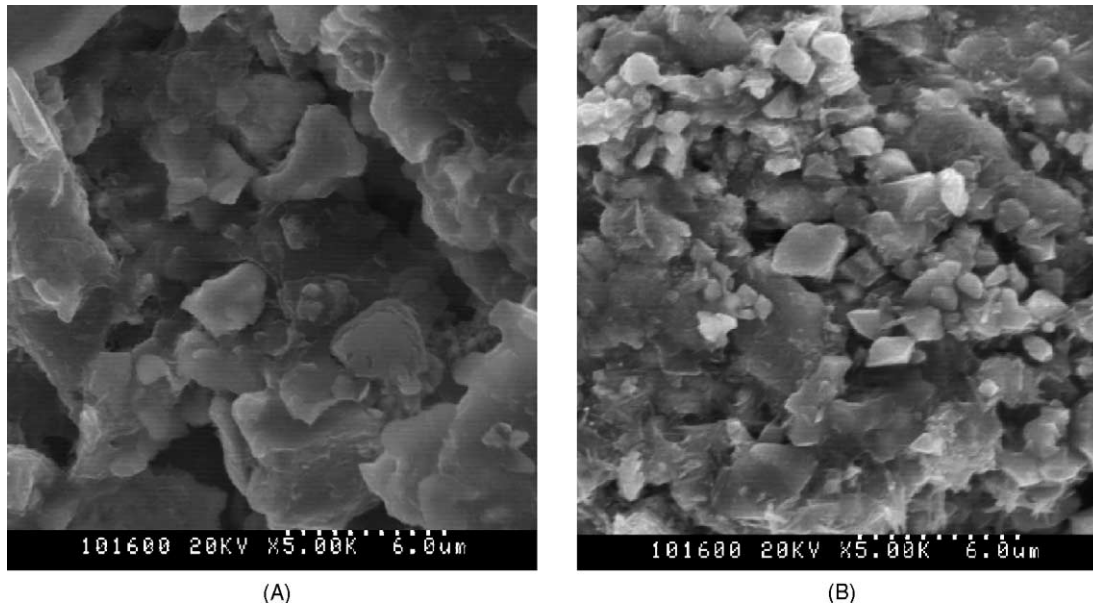


Fig. 8. Micrographs of anodes of Ni/MH batteries charged by DC and pulse current 1 C charge–discharge after 200 cycles: (A) pulse charge at 1 C ($t_p = 5$ s and $t_n = 1$ s) for 72 min and then discharged at the constant current of 1 C down to 1.0 V, (B) DC charge at 1 C for 72 min and then discharged at the constant current of 1 C down to 1.0 V.

4. Conclusions

The pulse charging is an effective approach to lower the internal pressure of battery during charge and overcharge, moreover, the appropriate frequency is $t_p = 5$ s and $t_n = 1$ s in our experiments. Pulse charging can also slowdown the capacity fade rate at the same charge–discharge rate and prolong the cycling lifetime of battery.

Acknowledgements

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