Journal of Thermal Analysis and Calorimetry, Vol. 58 (1999) 413-419

IN-SITU STUDY OF CHARGE AND DISCHARGE OF Ni-MH BATTERY USING THE COMBINED METHOD OF ELECTROCHEMISTRY AND MICROCALORIMETRY

Z. L. Zhang[1*], *M. H. Zhong*[1], *F. M. Liu*[1], *F. P. Zhong*[2] *and F. Wu*[2]

[1]Institute of Chemistry, Academia Sinica, Beijing 100080
[2]National Engineering Development Center of High Technology Energy-Storage Materials Zhongshan, Guangdong528437, P. R. China

Abstract

An apparatus to study the battery system has been set up. The thermal effects of charge and discharge of Ni–MH batteries have been studied. The calorimetric measurements indicate that the net heat dissipation during charging is larger than that during discharging. It is observed that the ratio of heat dissipation to charging energy varies with charging capacity, and almost 90 percent of charging energy is lost as heat dissipation near the end of the charging process at 97.7 mA. A jump of thermal curve near the end of discharge due to a secondary electrode reaction has been observed.

Keywords: combined method, Ni–MH battery, heat dissipation

Introduction

Ni–MH battery is a newly developed environmentally safe secondary battery with high energy density, long cycle life and overcharge and reversal protection mechanisms. Some advantages of replacing the cathode electrode material in Ni–H_2 battery with MH include the low interior pressure of the cell and the decreased rate of self-discharge. However, there are also several shortcomings. The self-discharge rate of the battery, for example, is still high; the heat, dissipation during the charging process is significant and the voltage is very low when discharging at high rate. In addition, some new problems emerged. For example, the material storing H_2 is not very stable and its capacity is limited. The solution to these problems relies on the understanding the processes occurring during the charge and discharge of the battery.

Since the significant thermal effects of charging and discharging a battery, microcalorimetry is very efficient to study both processes of charging and discharging a battery and self-discharge of a battery. With the calorimetric signal-time curve, it is possible to disclose the interior mechanisms of charging and discharging processes. Actually, there are several reports in the literature using microcalorimetry to study

* Author to whom all correspondence should be addressed.

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

both primary and secondary batteries [1–7]. The electrochemical parameters are very important to any practical applications, and what is more, the combination of electrochemical study with in-situ microcalorimetric measurement will certainly throw new light on the very system. The purpose of this work is to set up an apparatus of the combined method, to study the thermal effects of Ni–MH battery during the charging and discharging processes, to understand the charging and discharging mechanisms and to disclose the relationship between the rate of heat dissipation and the rate of charge and discharge of the battery.

Experimental

Materials

Ni–MH batteries were provided by Zhongshan Sunlite Hi-Tech. Co. These batteries (AA type) are cylindrical, approximately 1.4 cm dia. and 5.0 cm long, with a capacity of 1.1 Ah.

Apparatus

The experimental system has been set up and its reliability has been tested. The apparatus consisted of a microcalorimeter, electric circuit, resistors, an electric constant current source, a 150B microammeter and a potentiometer.

The Calvet microcalorimeter used in this work is the same as the one used in a previous work [8].

Experimental procedure

A resistor, as the calibration heater, and a sample battery were introduced into the measuring cell and connected to the electronic circuit system. The generation of heat caused by the wire during current drain and recharging the battery was negligible.

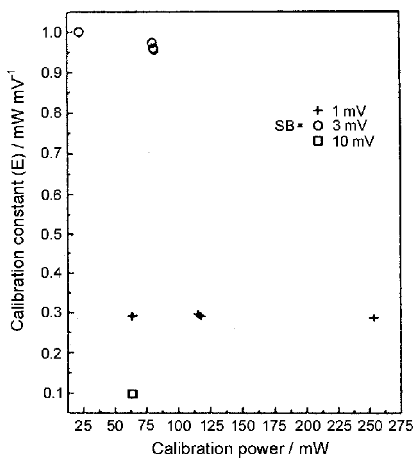

Fig. 1 Calibration constants of the calorimeter at various sensitivities

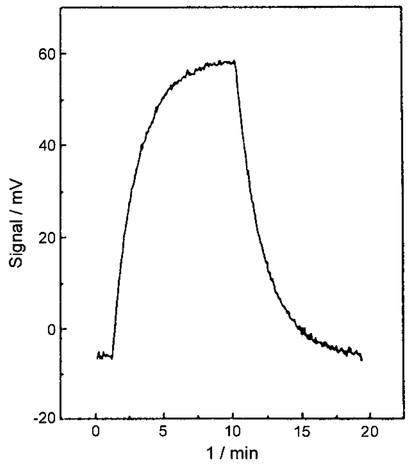

Fig. 2 Calibration of the Calvet microcalorimeter

Conduction of heat by the wire between the room and the calorimeter was expected to be negligible because of the length in contact with the thermostat above the calorimeter measuring cell. The calorimeter was calibrated using electric power and the results at different sensitivities are given in Figs 1 and 2.

Before the experiment, the battery was totally discharged. Then, as the first part of this work, the battery was recharged at the very low rate (2 mA) for about 15 min and then stopped for about 30 min. This charge and rest circle were maintained for 2.5 h. The electrical current was then increased to 50 mA and the battery was charged in the same way as before. The ratio of the net heat dissipation to the charging energy is given in Fig. 3. The corresponding charging capacity is the average between the measurements at the beginning and at the end of each period.

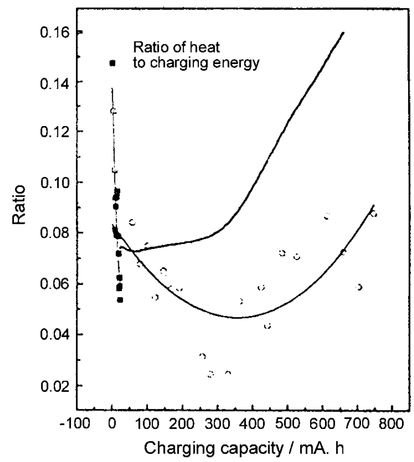

Fig. 3 Ratio of the net heat dissipation to the charging energy at the various charging rates
■ – charge at 2 mA; o – charge at 50 mA; (–) charge at 97.7 mA

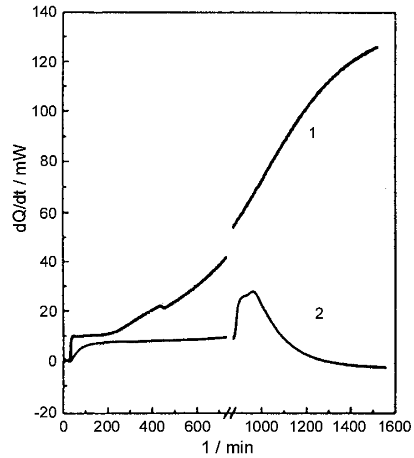

Fig. 4 Net heat dissipation during the charging process at 97.7 mA and the discharging process at the load of 10 Ohm. 1 – charging at 97.7 mA; 2 – discharging at load of 10 Ohm

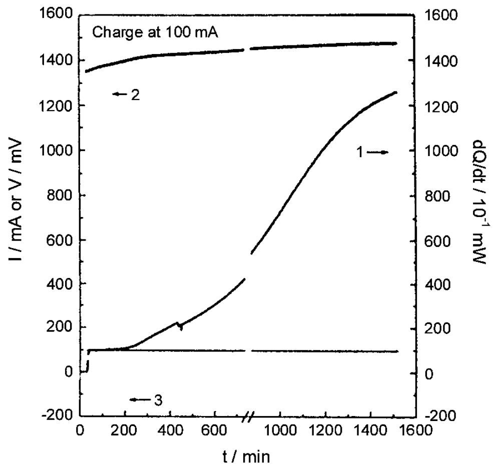

Fig. 5 Current, voltage and net heat dissipation during the charging process at 97.7 mA 1 – d*Q*/d*t*/10^{-1} mW; 2 – voltage/mV; 3 – current/mA

After discharging the battery totally at the load of 26 Ω, the results of which are given in Fig. 9, we charged the battery at the current of 97.7 mA continuously, then discharged the battery at the load of 10 Ω. The results are given in Figs 5–8.

All electrochemical and calorimetric experiments were performed at room temperature. The calorimetry results and the corresponding electrochemistry data were obtained with the experiment system interfaced with an IBM compatible computer.

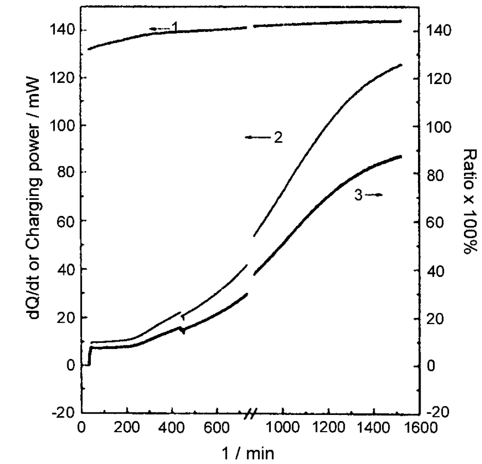

Fig. 6 Net heat dissipation, charging power and the ratio between them during the charging process at 97.7 mA. 1 – charging power; 2 – d*Q*/d*t*; 3 – ratio of heat to charging power

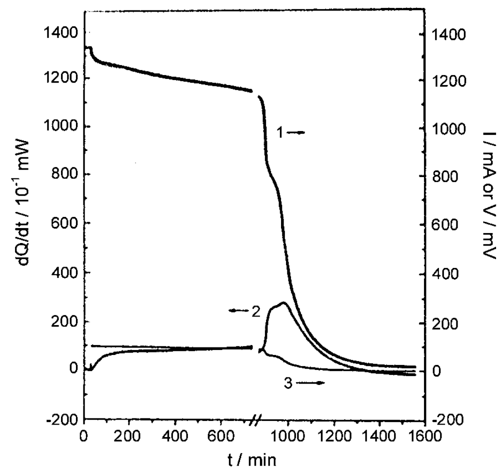

Fig. 7 Current, voltage and net heat dissipation during the discharging process at the load of 10 Ohm. 1 – voltage/mV; 2 – d*Q*/d*t*/10^{-1} mW; 3 – current/mA

Results and discussion

Heat dissipation during the charge and discharge of the battery

The results are given in Figs 3–9. It is observed that during both the charge and discharge, there exists net heat dissipation. As to the charge of the battery at the constant currents, the ratio of heat dissipation to the charging energy decreases firstly and then increases with the charging time at low charging rate and there exists a

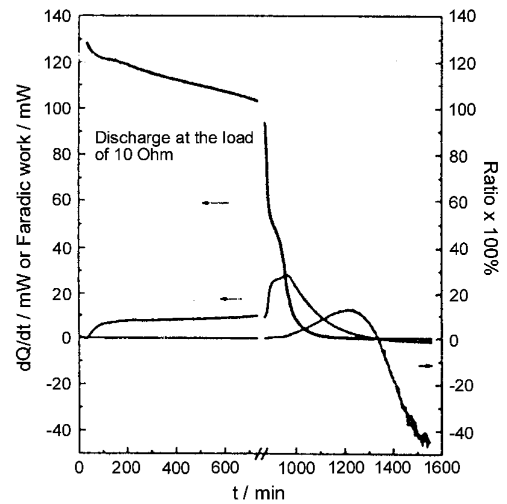

Fig. 8 Net heat dissipation, output power and the ratio between them during the discharging process at the load of 10 Ohm. 1 – dQ/dt; 2 – output power; 3 – ratio of heat to output power

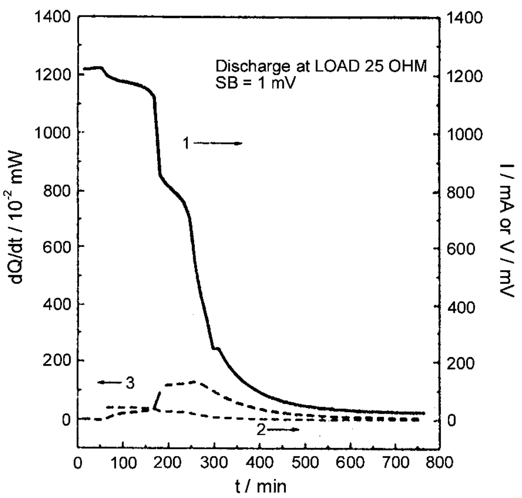

Fig. 9 Current, voltage and net heat dissipation during the discharging process at the load of 26 Ohm. 1 – voltage/mV; 2 – current/mA; 3 – dQ/dt/10^{-2} mW

minimum. However, when charging at the current of 97.7 mA, there is a plateau before 30 percent charge of the full battery capacity and then the ratio increases sharply with the charging time followed by a decrease of the increasing rate of the ratio. The heat dissipation is about 90 percent of the charging energy near the end of charging process, which may be attributed to the formation of β-MH and the catalyzed recombination of hydrogen and oxygen (Figs 3 and 6).

During the discharge of the battery, the net heat dissipation decreases with the decrease of the discharging rate and there is a plateau in the thermal curve too (Figs 7 and 9). The net heat dissipation during the discharge nearly at the same rate, is a little smaller than that during the charging within the plateau, but much less than that after the plateau, which indicates the different contributions of the formation of β-MH and the catalyzed recombination of hydrogen and oxygen during these processes (Figs 5 and 7).

Observed secondary electrode reaction

There is a special characteristic of the electrochemical and thermal curves of discharging (Figs 7, 8 and 9). When the battery has almost totally been discharged, there is a jump of the thermal curve, and the electrochemical curve also indicates a plateau simultaneously.

The jump of the thermal curves of discharge is probably due to the participation in the electrode reactions of the additives in the electrolyte and/or electrode materials and/or the intermediate products of electrode reactions instead of the phase transfer of metal hydride based on its phase diagram, the residual capacity of the battery, and the jump of the oxidation/reduction potential at the very point. Figure 3, which indicates the initial large ratio of heat dissipation to the charging energy at low charging rate, provides another basis for the above speculation.

Conclusions

This work has set up an apparatus and studied thermal effects of the charge and discharge of Ni–MH battery. It is observed that the net heat dissipation during charging is much larger than that of discharging after the plateau due to the different thermal effects of the cathode processes, the another Faradaic processes and the significant contribution of the catalyzed recombination of H_2 and O_2 during the charging process, which increases with the charging capacity. There exists a minimum of the ratio of the heat dissipation to the charging energy as to the ratio-charging capacity curve at the low charging rate.

The thermal curves of the discharge of battery show that there exists a secondary electrode reaction in the battery with a large enthalpy change. The very observation indicates that the combined method is very efficient to study the battery system.

References

1 O. A. Mashkin, Y. V. Kuzminskii and Y. A. Maletin, J. Power Sources, 34 (1991) 175.
2 E. S. Takeuchi, S. M. Meyer and C. F. Holmes, J. Electrochem. Soc., 137 (1990) 1665.
3 D. F. Untereker, ibid., 125 (1978) 1907.
4 F. B. Tudron, ibid., 128 (1981) 516.
5 Z. Mao, A. Visintin, S. Srinivasan and A. J. Appleby, ibid., 139 (1992) 985.
6 A. Visintin, S. Srinivasan, A. J. Appleby and H. S. Lim, J. Appl. Electrochem., 22 (1992) 409.
7 A. Vinsintin, A. Anani, S. Srinivasan, A. J. Appleby and H. S. Lim, ibid., 25 (1995) 833.
8 Z. L. Zhang, X. Z. Sun, W. X. Zhou, L. Q. Zhang, B. Li, M. G. Wang, B. Z. Yan and F. Tan, J. Thermal Anal., 45 (1995) 99.