

Short Communication

Heat dissipation from a Ni–MH battery during charge and discharge with a secondary electrode reaction

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Abstract

Microcalorimetry has been examined as an efficient method for studying the thermal effects of charge and discharge of Ni–MH batteries. The calorimetric measurements indicate that the net heat dissipation during charging is larger than that during discharging at the same rate. It is observed that the ratio of heat dissipation to charging energy varies with charging capacity, and almost 90% of the charging energy is lost as heat dissipation near the end of the charging process at a rate of 97.7 mA. A jump in the thermal curve near the end of discharge due to a secondary electrode reaction has been observed. © 1998 Elsevier Science S.A.

Keywords: Ni–MH battery; Charge and discharge; Heat dissipation

1. Introduction

Microcalorimetry is a very efficient method for studying the charging, discharging and self-discharge of batteries. There have been several reports of the use of microcalorimetry to study both primary and secondary batteries [1]. For example, Takeuchi et al. [2] have shown that microcalorimetry can predict the shelf-life of thionyl chloride cells based on the relationship between the heat dissipation and the rate of self-discharge. Untereker [3] have studied Li/I₂ and Zn/HgO cells and demonstrated a good agreement between their model to anticipate the energy loss and the corresponding experimental results. Tudron [4] have investigated the thermal effects of miniature alkaline cells under load using dynamic microcalorimetry to explain the discharge mechanisms. Mao et al. [5] and Visintin et al. [6,7] have performed systematic research on secondary batteries, especially the Ni–H₂ system. They pointed out that the reaction of hydrogen with the nickel oxide electrode is responsible for self-discharge and proposed the storing of hydrogen as hydride to minimize the self-discharge rate.

The nickel/metal-hydride (Ni–MH) battery is a newly developed, environmentally safe, secondary battery with

high specific energy, long cycle life, and overcharge and reversal protection mechanisms. Some of the advantages of replacing the cathode electrode material in the Ni–H₂ system with MH include the low interior pressure of the cell and the decreased rate of self-discharge. Nevertheless, 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 output voltage is very low when discharging at a high rate. In addition, some new problems emerged. For example, the material that stores the H₂ is not very stable and its capacity is limited. The solution to these problems relies on understanding of the processes that occur during the charge and discharge of the battery.

The purpose of this work is to study the thermal effects of Ni–MH batteries during 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.

2. Experimental

2.1. Materials

Ni–MH batteries were provided by Zhongshan Sunlite Hi-Tech Co. These batteries (AA type) are cylindrical

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(approximately 1.4 cm in diameter, and 5.0 cm long) with a capacity of 1.1 Ah.

2.2. Apparatus

The experimental system consisted of a microcalorimeter (Calvet), electric circuit, resistors, an electric constant current source, a 150B microammeter, and a potentiometer. The Calvet microcalorimeter is the same as the that used in previous work [8].

2.3. Experimental procedure

A resistor (used 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. 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. 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 phase of this study, the battery was recharged at a very low rate (2 mA) for about 15 min and then stopped for about 30 min. This charge and rest circle was 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

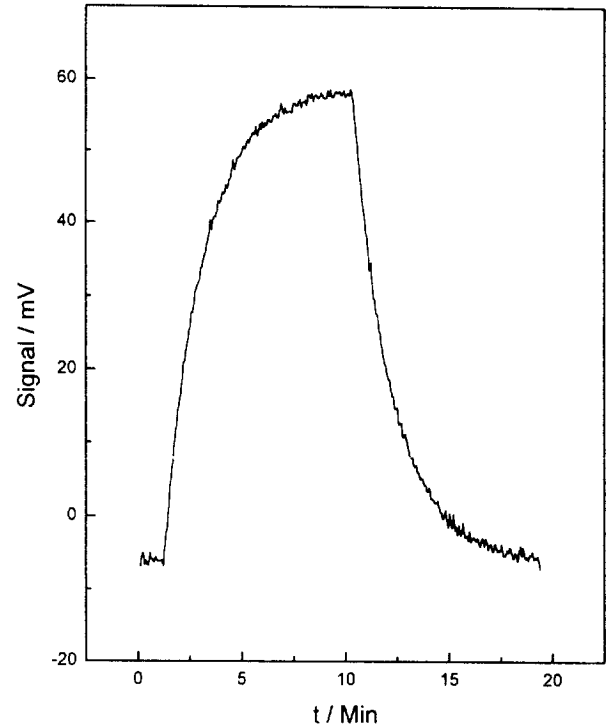


Fig. 2. Calibration of Calvet microcalorimeter.

measurements at the beginning and at the end of each period.

After discharging the battery totally under a load of 26 Ω, the battery was charged at a current of 97.7 mA continuously, then discharged under a load of 10 Ω.

All electrochemical and calorimetric experiments were performed at room temperature. The calorimetry results

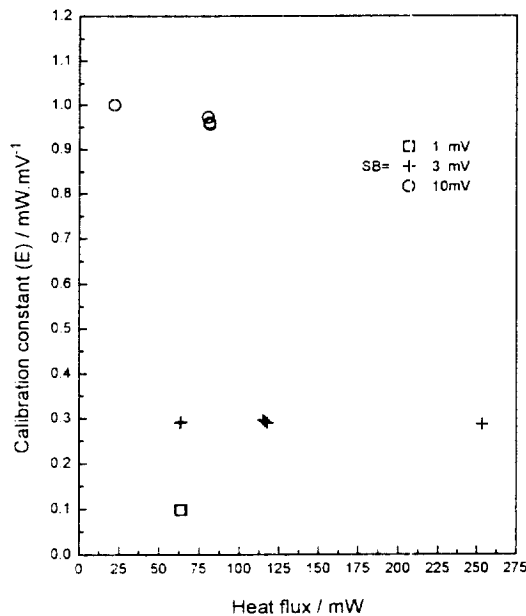


Fig. 1. Calibration constants of calorimeter at various sensitivities.

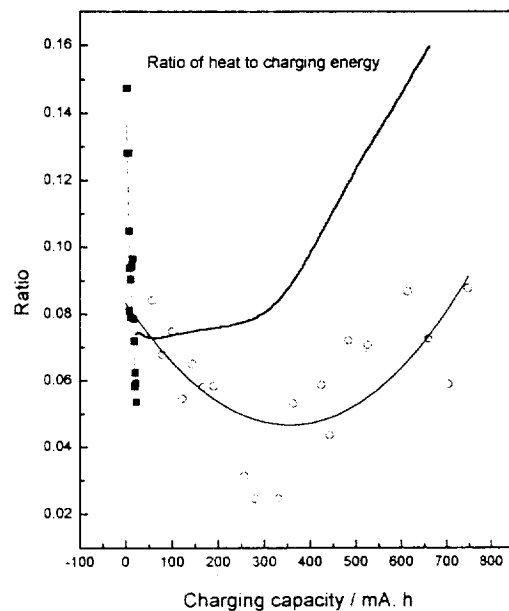


Fig. 3. Ratio of net heat dissipation to charging energy at various charging rates: (■) Charge at 2 mA; (○) Charge at 50 mA; (—) Charge at 97.7 mA.

and the corresponding electrochemistry data were obtained with the experiment system interfaced with an IBM compatible computer.

3. Results and discussion

3.1. Heat dissipation during charge and discharge of the battery

Data show that there exists net heat dissipation during both the charge and discharge processes (Figs. 3–9). For battery charging at a low-rate constant currents, the ratio of heat dissipation to the charging energy decreases initially and then increases with the charging capacity and there exists a minimum. At higher rates, e.g., 97.7 mA, there is a plateau before 30% charge of the full battery capacity and then the ratio increases sharply with the charging time followed by a decrease in the increasing rate of the ratio. The heat dissipation is about 90% of the charging energy near the end of the charging process, see Figs. 3 and 6.

During discharge of the battery, the net heat dissipation decreases with decrease of discharging rate and there is a plateau in the thermal curve, see Figs. 7 and 9. The net heat dissipation during the discharge is slightly smaller than that during charging within the plateau, but is much less after the plateau, see Fig. 4.

Concerning the minimum in Fig. 3, we suggest that there are at least three different kinds of reactions that contribute significantly to the net heat dissipation. The rate of the first reaction decreases rapidly with charging time

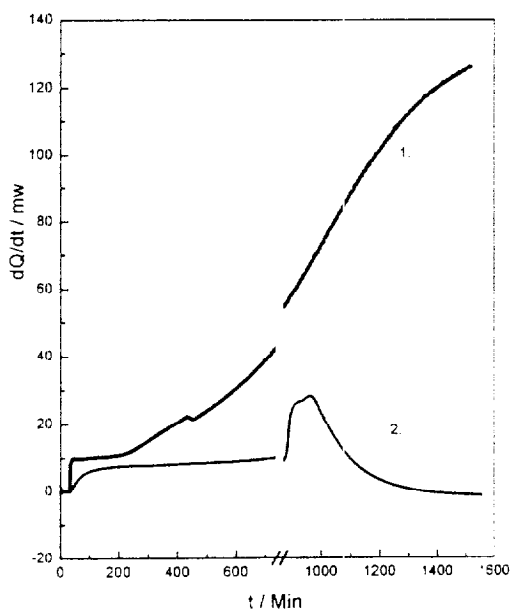


Fig. 4. Net heat dissipation during charging process at 97.7 mA and discharging process under a load of 10 Ω. (1) (—) Charging at 97.7 mA; (2) (—) Discharging at load of 10 Ω.

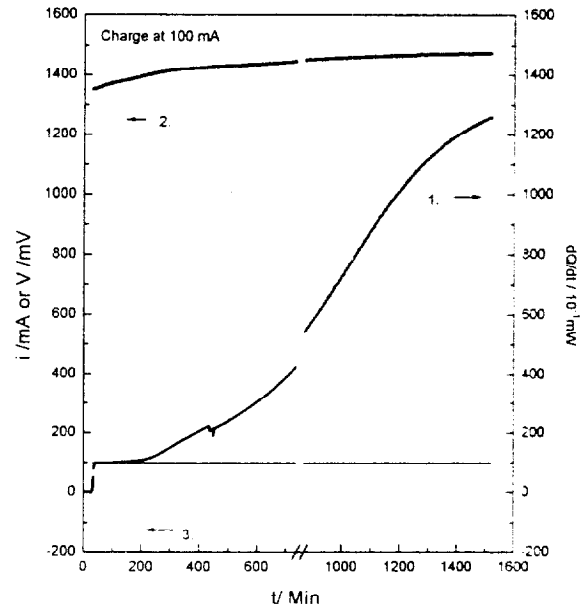


Fig. 5. Current, voltage and net heat dissipation during charging process at 97.7 mA. (1) (—) $dQ/dt \cdot 10^{-1}$ mW; (2) (—) Voltage/mV; (3) (—) Current/mA.

because of the low concentrations of the reactants; the rate of the second reaction increases sharply with charging capacity, for example, the catalyzed recombination of hydrogen and oxygen; and the rate of the third reaction does not change dramatically during the charging process.

The battery system is very complicated and there are faradaic and co-existing non-faradaic processes. During the

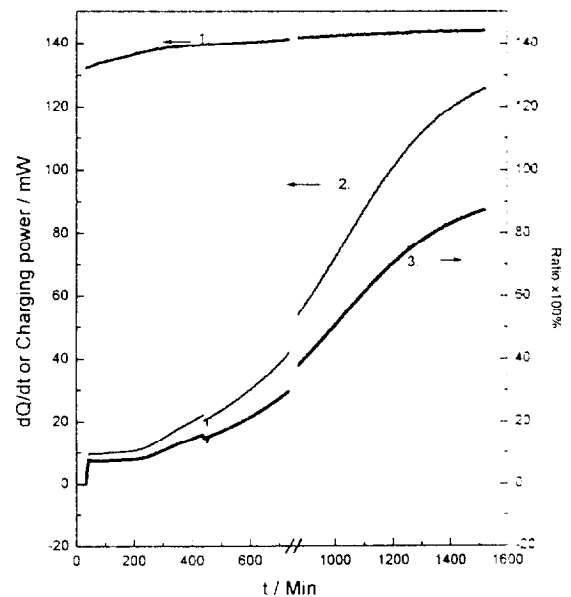


Fig. 6. Net heat dissipation and charging power, as well as the ratio between them, during charging process at 97.7 mA. (1) (—) Charging power; (2) (—) dQ/dt ; (3) (—) Ratio of heat to charging power.

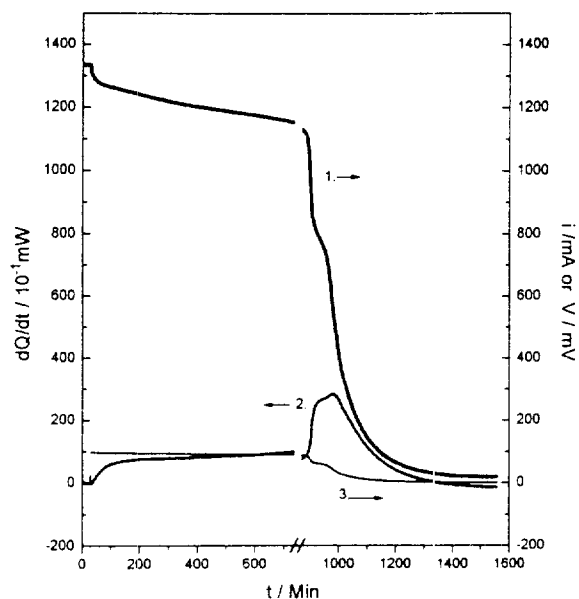
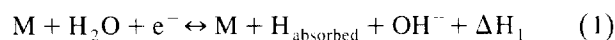


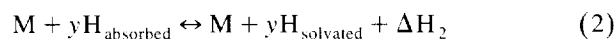
Fig. 7. Current, voltage and net heat dissipation during discharging process under a load of 10 Ω. (1) (—) Voltage/mV; (2) (—) $dQ/dt/10^{-1}$ mW; (3) (—) Current/mA.

charging and discharging processes, the following processes take place at the cathode

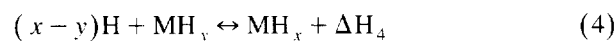
1. Charge transfer:



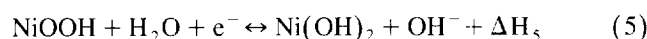
2. Solvation, diffusion and chemical reaction of hydrogen:



3. Phase transfer of metal hydride:



The following reaction takes place at the anode:



ΔH denotes the corresponding enthalpy change.

The total heat dissipation during charging, ΔH_{net} , should be the sum of ΔH_1 , ΔH_2 , ΔH_3 , ΔH_4 , and ΔH_5 plus the heat due to the internal resistance, the polarizing potential, and non-faradaic processes in the battery, $\Sigma\Delta H_j$. It is proposed that, during the final period of charging, the net heat is mainly due to the formation of β -MH and non-faradaic processes, for example, the catalyzed recombination of H_2 and O_2 . Actually, our most recent results of gas phase composition analysis in the battery indicated that the oxidation of hydrogen gas on the anode is probably the major mechanism of the recombination.

During discharging, the reverse of reactions 1–5 is endothermic. The contribution of the catalyzed recombination of H_2 and O_2 to the net heat dissipation during discharging is smaller than that during charging. Thus, the net heat dissipation of discharging the battery is much smaller than that of charging the battery. Indeed, an appar-

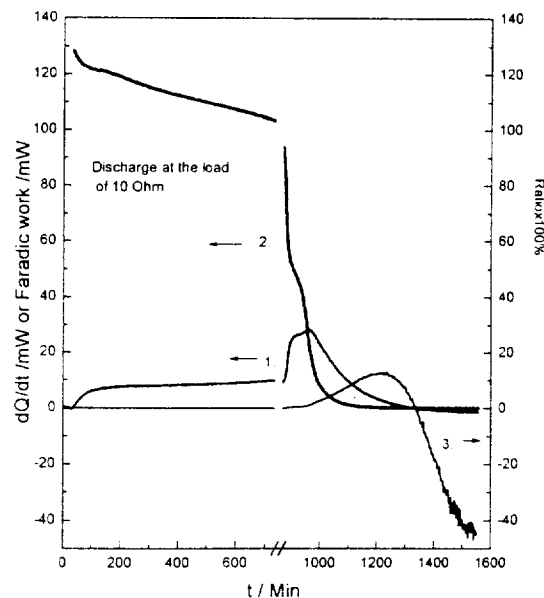


Fig. 8. Net heat dissipation, output power, and ratio between them, during discharging process under a load of 10 Ω. (1) (—) dQ/dt ; (2) (—) Output power; (3) (—) Ratio of heat to output power.

ently endothermic discharge process has been observed, see Fig. 8.

3.2. Observed secondary electrode reaction

A special characteristic has been observed in the electrochemical and thermal curves of discharge, see Figs. 7–9. When the battery has been almost totally discharged,

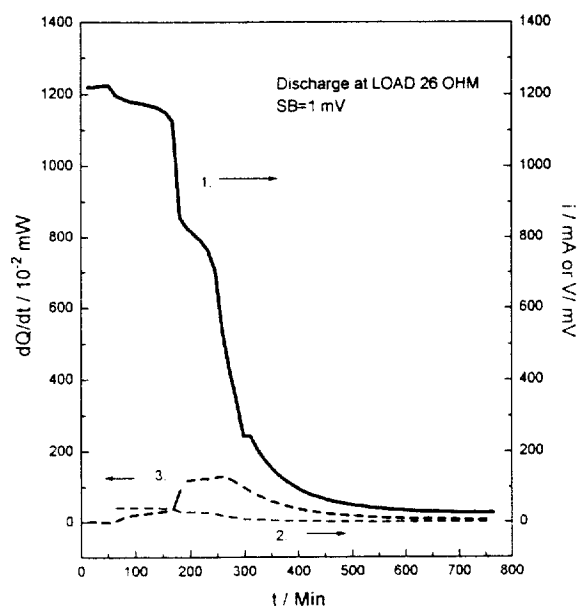


Fig. 9. Current, voltage and net heat dissipation during discharging process under a load of 26 Ω. (1) (—) Voltage/mV; (2) (—) Current/mA; (3) (—) $dQ/dt/10^{-2}$ mW.

there is jump in the thermal curve, and each of the electrochemical curves exhibit a plateau.

The jump in the thermal curves of discharge is probably caused by the participation in the electrode reactions of additives in the electrolyte and the electrode materials and/or by the intermediate products of electrode reactions instead of phase transfer of the metal hydride. To determine the exact mechanisms of the parasitic side reactions, a series of studies on the composition of the electrodes and the electrolyte should be carried out at different charging and discharging stages of the battery.

4. Conclusions

This work has studied thermal effects of the charge and discharge of the Ni–MH battery system. It is observed that the net heat dissipation during charging is significantly larger than that of discharging after the plateau due to the different thermal effects of the cathode processes, the anode 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. A minimum exists in the ratio of the heat dissipation to the charging energy at low charging rates. The discharging

process is endothermic when the battery is almost totally discharged, as the thermal effects of the electrode processes cannot be completely offset by the heat generation caused by the internal resistance, polarization and non-faradaic processes near the complete discharge of the battery.

The thermal curves of the discharge of battery show that there exists a secondary electrode reaction in the battery with a large enthalpy change.

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