THERMAL BEHAVIOR OF NICKEL/METAL HYDRIDE BATTERY DURING CHARGING AND DISCHARGING

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This work discusses thermal behavior of Ni/MH battery with experimental methods. The present work not only provides a new way to get more exactly parameters and thermal model, but also concentrates on thermal behavior in discharging period. With heat generation rate gained by experiments with microcalorimeter, heat transport equations are set up and solved. The solutions are compared with experiment results and used to understand the reactions inside the battery. Experiments with microcalorimeter provide more reliable data to create precise thermal model.

Keywords: *microcalorimeter, Ni/MH battery, thermal behavior*

Introduction

Development of electric vehicles (EV) and hybrid electric vehicles (HEV) boosts battery technology research. The battery with high specific energy, high rate capability, long cycle life, and low environmental impact as power storage device is a general research subject. At present, Ni/MH battery is a popular choice for EV and HEV power storage device. As volume and mass in a vehicle are rather limited, the battery system has to be smaller in order to take up less space. Battery failure could also result from excessive temperature rise and steeper temperature gradient within a battery. In order to avoid potential problems caused by temperature rise, information about heat generation is required.

Thermal model for the battery could help to analyze the impact on performance owing to need of a thermal management for the battery [1–3]. Several methods were used to simulate the battery behavior like computational fluid dynamics (CFD) and finite element methods (FEM) [4]. Bernardi [5] had set up a general energy balance for battery systems with assumption of uniform heat generation. After that Chen and Evans [6, 7] developed several two-dimensional and three-dimensional thermal models, and presented some calculation methods for model parameters. Shi [8] studied rapid charging of spirally cylindrical nickel/metal hydride battery with thermal model. Wu [9] validated the cooling effect of auxiliary cooling device with thermal model and showed the state of charge, open circuit voltage, internal resistance, power and available energy changed with battery temperature rise. Sato [10, 11] examined many ways of heat generation for electric vehicle battery and found that the battery's temperature rise was usually caused by heat generation due to electrochemical reactions and Joules effect. The mathematical simulation of heat transport in the battery had high efficiency and fairly low cost compared to laboratory experiments, moreover, the agreement between theoretical and experimental values was good in many earlier works.

Many papers concentrated on thermal behavior in charging period. Although heat generation in discharging period is not as serious as that in charging period, we should know about the period clearly to prevent potential problems. In this work, we will focus on heat generation not only in charging period but also in discharging period and develop a model to discuss the results.

Experiments

The experiment uses cylindrical Ni/MH battery with spirally design, rating capacity of 8 Ah and actual capacity of 7.5 Ah after cycles. The battery includes electrodes, electrolyte and separator and is assumed to be axial symmetric. Some details are in Table 1.

The tested battery is installed in a special device, which protects the battery from short circuit. During the experiment, a microcalorimeter with a quartz frequency thermometer is used to measure the heat capacity and quantity of heat. The whole device is in the microcalorimeter, as shown in Fig. 1. In discharging experiments, the Ni/MH battery is charged in 1C (C is abbreviation for capacity) rate to 100 and 90% (State of Charge, SOC for short) of its capacity first, and

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Table 1 Some parameters of tested battery

Parameters	Values
r, radius/m	0.01609
h, height/m	0.0605
R, resistance/mΩ	3.0
M, mass/kg	0.18909
V, volume/m^3	0.000049205

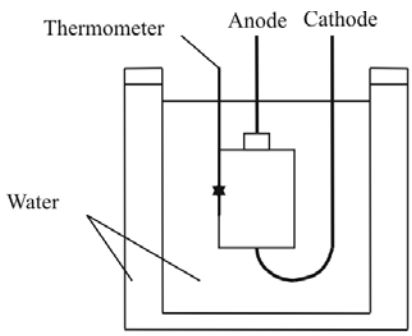

Fig. 1 Experiment device system

then the battery is discharged in 10C, 15C and 20C rate. In charging experiments, the Ni/MH battery is charged to fixed SOC (State of Charge) in 1C rate first: 0, 30, 50, 70, 90, 100%. Then the battery is charged in 1C, 3C and 5C rate to 150% of its actual capacity. The discharging and charging process is controlled by an Arbin instrument, and data are saved by the program on a PC.

Results and discussion

Results

Charge

Heat generation rates are shown in Fig. 2.

The two curves of SOC 100% and SOC 90% in each figure are quite similar. Therefore, test result of SOC 90% is chosen for curve fitting to get a function that describes the charging process. For curve of SOC 90%, the quartz frequency thermometer shows the surface temperature rises after 1C, 3C and 5C rate charging are 2.289, 2.093 and 1.956°C.

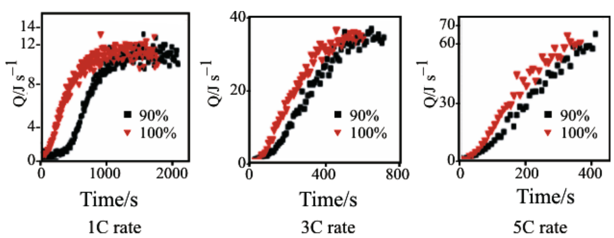

Fig. 2 Heat generation rate of charging battery

Curve of SOC 90% is divided into normal section and overcharging section for curve fitting to get the expression. In normal charging section, heat generation rate is slowly increasing. According to [8, 10, 11], the increase is caused by reaction heat and joule heat. In some cases, heat generation rate could be assumed constant, because the slope is small. In overcharging section, recombination whereby the generated oxygen and hydrogen return to water contributes to Q [11]. The heat generation rate in overcharging period is considerable and keeps increasing.

The expressions of Q are:

For 1C

$$Q=\begin{cases}1.25747+0.000158t & 0<t\le 320\\ 11.50979-28.884\cdot 0.99743^{t} & 320<t\le 2160\end{cases} \quad (1)$$

For 3C

$$Q=\begin{cases}4.66553+0.00253t & 0<t\le 102\\ 51.09361-56.32\cdot 0.9982^{t} & 102<t\le 720\end{cases} \quad (2)$$

For 5C

$$Q=\begin{cases}11.4117+0.01303t & 0<t\le 67\\ 8.10951-0.12909t & 67<t\le 432\end{cases} \quad (3)$$

Expressions of SOC 100% can be attained by curve of SOC 90% through linear transform:

$$t_{100\%}=t_{90\%}-\frac{360}{\text{rate}}$$

in which

$$\text{rate}=1,\ 3,\ 5 \quad (4)$$

where $t_{100\%}$ denotes charging time of the battery in SOC 100%, $t_{90\%}$ denotes charging time of the battery in SOC 90%.

According to reaction kinetics, reaction rate differential equation of first order reaction is:

$$-\frac{\mathrm{d}c}{\mathrm{d}t}=kc \quad (5)$$

where c denotes concentration of reactant.

For a reaction with reaction ΔH,

$$-\frac{\mathrm{d}}{\mathrm{d}t}\frac{\mathrm{d}(\Delta Hc)}{\mathrm{d}t}=k\frac{\mathrm{d}(\Delta Hc)}{\mathrm{d}t} \quad (6)$$

$$-\frac{\mathrm{d}Q}{\mathrm{d}t}=kQ \quad (7)$$

and integral form is:

$$Q=A-A\mathrm{e}^{-kt} \quad (8)$$

where A is a constant.

In overcharging period, expressions of Q for 1C and 3C rate charging can be written as:

$$\text{For 1C}\quad Q = 11.50979 - 28.884 \cdot 0.99743^{t} = 11.50979 - 11.50979e^{-0.002573308(t-310)} \qquad (9)$$

$$\text{For 3C}\quad Q = 51.09361 - 56.32 \cdot 0.9982^{t} = 51.09361 - 51.09361e^{-0.001801621(t-99)} \qquad (10)$$

The equations above are similar with theoretical equation. Therefore, it is reasonable to believe that the overcharge reaction of 1C and 3C rate charge is a first order reaction or pseudo first order reaction.

Because diffusion is the rate-determining step under high rate charging and the heat conductivity is limited inside the battery. Therefore, heat generation rate may not help to determine the reaction order of 5C rate higher rate charging.

Discharge

Heat generation rates in discharging experiments are shown in Fig. 3.

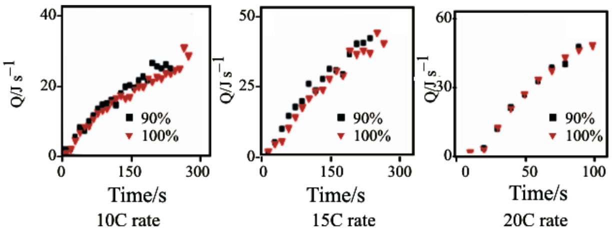

Fig. 3 Heat generation rate of discharging battery

The two curves of SOC 100% and SOC 90% in each figure are also similar. Curve of SOC 100% is chosen for curve fitting to get a function that describes the discharging process.

For curve of SOC 100%, the quartz frequency thermometer shows the surface temperature rises after 10C, 15C and 20C rate discharging are 0.887, 0.603, and 0.673°C.

During discharging period joule heat should play an important role and remain constant according to theoretical analysis, but heat generation rates keep increasing. This may be caused by increased internal resistance which also makes voltage down.

The expressions of the curves are gained by linear fitting. Expressions of Q are:

$$\text{For 10C}\quad Q = 2.55303 + 0.09929t \qquad (11)$$

$$\text{For 15C:}\quad Q = 0.83639 + 0.2585t \qquad (12)$$

$$\text{For 20C:}\quad Q = 3.96375 + 0.40097t \qquad (13)$$

Thermal model

Two-dimensional model is developed to analyze the thermal behavior. The battery is assumed to be axial symmetric, so the heat transport equation is:

$$MC_{p}\frac{\partial T}{\partial t} = V\frac{1}{r}\frac{\partial}{\partial r}\left(k_{r} r\frac{\partial T}{\partial r}\right) + V\frac{\partial}{\partial z}\left(k_{z}\frac{\partial T}{\partial z}\right) + Q \qquad (14)$$

$$\text{IC: } T(r,z,0) = T_{0} \qquad (15)$$

$$\text{BC: } -k_{r}\left.\frac{\partial T}{\partial r}\right|_{r=R_0} = h\left(T\big|_{r=R_0} - T_{\infty}\right),$$

$$-k_{z}\left.\frac{\partial T}{\partial z}\right|_{z=0,H} = h\left(T\big|_{z=0,H} - T_{\infty}\right), \qquad (16)$$

C_p is average heat capacity, which is measured by microcalorimeter before discharging and assumed constant; k_r (k_z) is thermal conductivity of the battery in r-direction (z-direction); T_0 denotes initial temperature of the battery before the experiment; h denotes heat transfer coefficient. Values are shown in Table 2.

T_∞ is ambient temperature, it was increasing during discharging process, the value is estimated by:

- Charge

$$\text{For 1C}\quad T_{\infty} = 24.055 + 2.289 \cdot \frac{t}{2160} \qquad (17)$$

$$\text{For 3C}\quad T_{\infty} = 24.055 + 2.093 \cdot \frac{t}{720} \qquad (18)$$

$$\text{For 5C}\quad T_{\infty} = 24.055 + 1.956 \cdot \frac{t}{432} \qquad (19)$$

- Discharge

$$\text{For 10C}\quad T_{\infty} = 13.4 + 0.887 \cdot \frac{t}{268.8} \qquad (20)$$

$$\text{For 15C}\quad T_{\infty} = 13.4 + 0.603 \cdot \frac{t}{172.8} \qquad (21)$$

Table 2 Values of parameters in thermal model

Parameters	Values
Heat capacity, C_p/J kg^{-1} °C^{-1}	301.206
Thermal conductivity in r-direction, k_r/J s^{-1} m^{-1} °C^{-1}	0.74 [8]
Thermal conductivity in z-direction, k_z/J s^{-1} m^{-1} °C^{-1}	0.85 [8]
Surface area, A/m^2	0.00769
Initial temperature, T_0/°C	13.44 (discharge), 24.055 (charge)

$$\text{For 20C } T_\infty = 13.4 + 0.673 \cdot \frac{t}{144} \quad (22)$$

According to Newton's law of cooling:

$$Q = hA\Delta T \quad (23)$$

ΔT denotes temperature difference between battery wall and ambient temperature.

The experiment shows that ΔT is smaller than 1°C, so we assume it to be constant for simplicity, 1°C. Heat transfer coefficient is expressed by:

$$h = \frac{Q}{A\Delta T} \quad (24)$$

Discussion

Charge

Solutions of equations for different rate charging at SOC 90% are shown in Fig 4, two-dimensional temperature profile in the *r*-direction and *z*-direction at the end of 1C, 3C and 5C rate charging. The results are compared in Table 3.

The inside temperatures of 3C and 5C rate charge are much higher than that of 1C rate charge, up to 75.81 and 85.44°C. The steep temperature gradient may be caused by low heat transfer coefficient of materials inside the battery, which is harmful to the battery and would affect the battery performance. After 1C rate charge the inside temperature is 30.823°C, the battery is under good working condition.

Surface temperature rises of SOC 90% by calculation are 2.286, 2.061 and 1.925°C. Comparing with the results of experiment, the calculated results match the experimental results very well.

The temperature distribution is non-uniform because the poor conductivity in *r*-direction limits the heat transfer during charging process. It is difficult to greatly improve the heat conductivity of the battery because it is related to materials inside the battery including electrodes, separators and so on. Therefore, high rate charge should be avoided in actual use. It may cause some damage to the battery.

Discharge

Solutions of equations for different rate discharging at SOC 100% are shown in Fig. 5, two-dimensional temperature profile in the *r*-direction and *z*-direction at the end of 10C, 15C and 20C rate discharging. The results are compared in Table 4.

Surface temperature of 15C rate discharging is lower than the others, a possible reason is 15C rate discharging generates less heat and there is not enough time for heat to get outside of the battery. Although heat generation in discharging period is not as

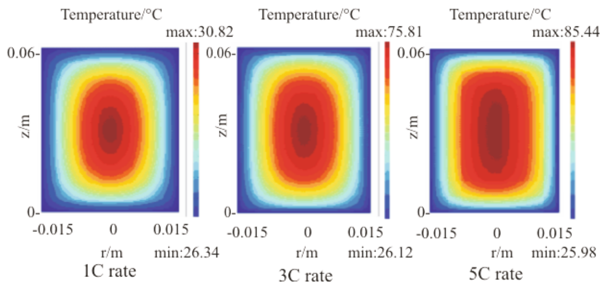

Fig. 4 Temperature distribution by calculation in tested battery after charging (red area has higher temperature than blue area)

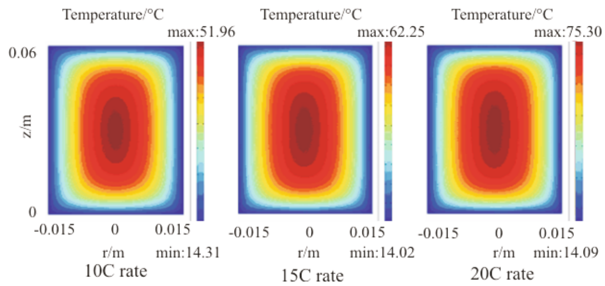

Fig. 5 Temperature distribution by calculation in tested battery after discharging (red area has higher temperature than blue area)

Table 3 Comparison of experiment and calculation

Rate temperature rise/°C		1C		3C		5C	
		experiment	calculation	experiment	calculation	experiment	calculation
SOC	90%	2.289	2.286	2.093	2.061	1.956	1.925
	100%	2.299	2.299	1.907	1.873	1.844	1.794

Table 4 Comparison of experiment and calculation

Rate temperature rise/°C		10C		15C		20C	
		experiment	calculation	experiment	calculation	experiment	calculation
SOC	90%	0.508	0.493	0.494	0.480	0.259	0.255
	100%	0.887	0.868	0.603	0.584	0.673	0.652

serious as that in charging period, the internal temperature is also high in high rate discharging. The experimental model shows that highest temperature inside the battery is 51.97°C after 10C rate discharging, 62.25°C after 15C rate discharging and 75.30°C after 20C rate discharging. As shown in Table 4, the calculated results are close to the experimental results. If we consider the internal resistance as a linear function of time, the model would be more accurate. Reaction rate in the battery during high rate discharging is determined by diffusion and mass transfer step. Internal resistance increases as transfer resistance goes up when discharging continues.

Conclusions

Thermal behavior of Ni/MH battery in charging and discharging process is studied with microcalorimeter. During normal charging, heat generation rate is slowly increasing. In overcharging process, the heat generation rate increases greatly because of the recombination reaction of oxygen and hydrogen. Heat generation rate is also considerable during high rate discharging just like that during overcharging. Two-dimensional model is developed to analyze the thermal behavior. The calculated results match the experimental results very well. The temperature distribution inside the battery is non-uniform because of the poor heat conductivity of the materials inside the battery. Therefore, high rate charging and discharging for a long time should be avoided.

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