Journal of Power Sources 184 (2008) 622–626

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

Thermal behavior of overcharged nickel/metal hydride batteries

Dahe Li, Kai Yang*, Shi Chen, Feng Wu

School of Chemical Engineering & Environment, Beijing Institute of Technology, Beijing 100081, China

ARTICLE INFO

Article history:
Received 16 January 2008
Received in revised form 15 March 2008
Accepted 18 March 2008
Available online 29 March 2008

Keywords:
Ni/MH battery
Thermal model
Microcalorimeter

ABSTRACT

This work provides a two-dimensional thermal model for cylinder Ni/MH battery. Thermal model is developed to analyze the thermal behavior of the battery when charged and overcharged. Quantity of heat and heat generation rate of the battery during charge and overcharge period are studied by quartz frequency microcalorimeter. Heat generation curve is fitted into a function, and heat transport equation is solved. Analysis with the model and experiment show that temperature rise is about 3 °C and difference between the model and the experiment is no more than 0.1 °C.

1. Introduction

Electric vehicles (EV) and hybrid electric vehicles (HEV) are becoming more attractive because of growing demand for power sources. EV and HEV require the battery with high specific energy, high-rate capability, long cycle life, and low environmental impact as power storage device, which boosts development of battery technology. At present, most research concentrated on Ni/MH and lithium/polymer battery because the two kinds of batteries are green and have good performance. Their performances are both sensitive to temperature change, temperature rise even caused some safety problems of lithium/polymer. Therefore, Ni/MH battery is a popular choice for EV and HEV power storage device. In order to avoid potential problems caused by temperature rise, information about heat generation is required.

It is reasonable to develop a thermal model for the battery to analyze the impact on performance when temperature is rising owing to the necessity of a thermal management for the battery [1–3]. Several methods are used to simulate the battery behavior like computational fluid dynamics (CFD) and finite element methods (FEM) [4]. Bernadi et al. [5] have 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 et al. [8] studied rapid charging of spirally cylindrical nickel/metal hydride battery with thermal model. Sato et al. [9,10] examined many heat generation ways 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. Wu et al. [11] 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. The mathematical simulation of heat transport in the battery has high efficiency and fairly low cost compared to laboratory experiments, moreover, the agreement between theoretical and experimental values was good in many earlier works.

Once the battery is overcharged, oxygen generated at positive electrode reacts with hydrogen at negative electrode, and considerable amount of reaction heat accompanies recombination. The working condition for the battery would be much worse if the battery were overcharged. As volume and weight in a vehicle are rather limited, the battery system has to be smaller in order to take up less space. Now that temperature is an important factor of the battery performance, the specific cooling device must be effective to avoid excessive temperature rise. We will discuss heat generation in both normal charge and extreme charge and develop a model for the whole process and discuss the model and the experiment results. We hope that some problems can be found like abnormal hot spots or areas to improve thermal management.

2. 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

* Corresponding author. Tel.: +86 10 68912528.
E-mail address: ykbit@bit.edu.cn (K. Yang).

0378-7753/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2008.03.059

Table 1
Some parameters of tested battery

Parameters	Values
R, radius (m)	0.01609
H, height (m)	0.0605
M, mass (kg)	0.18909
V, volume (m^3)	0.000049205

and is assumed to be axial symmetric. Some details are in Table 1.

The tested battery is installed in a special device, which is designed to protect the battery from short circuit. During the experiment, a microcalorimeter with a quartz frequency thermometer is used to measure the surface temperature of the battery and the heat generation rate. The whole set is in the microcalorimeter, as shown in Fig. 1. All data are recorded by a PC.

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

3. Results and discussions

3.1. Experiment results

The quartz frequency thermometer shows the surface temperature rises after 1C, 3C, and 5C rate charge are 2.714, 2.883, and 2.826 °C. Heat generation rates are shown in Figs. 2–4. Curves in the three figures are charged in 1C, 3C and 5C rate from SOC of 0, 30, 50, 70, 90, and 100%, respectively. It seems that in a certain charge rate, a curve is moving to the left as SOC increasing from 0 to 100%.

During normal charge process, heat generation rate is slowly increasing. Joule heat plays an important role in this period. When the battery is overcharged, curves become much steeper. Heat generated during overcharging takes a great part of total heat generation.

The curves in each figure are quite similar, so other curves can be expressed by curve of SOC 0% through linear transform:

$$t_{SOC} = t_{0\%} - \frac{3600}{\text{rate}}\text{SOC}, \qquad \text{SOC} = 30,\ 50,\ 70,\ 90,\ 100\%, \quad \text{rate} = 1,\ 3,\ 5 \tag{1}$$

where t_{SOC} denotes charging time of the battery in certain SOC; $t_{0\%}$ denotes charging time of the battery in SOC 0%. Therefore, test result of SOC 0% is chosen for curve fitting to get a function that describes

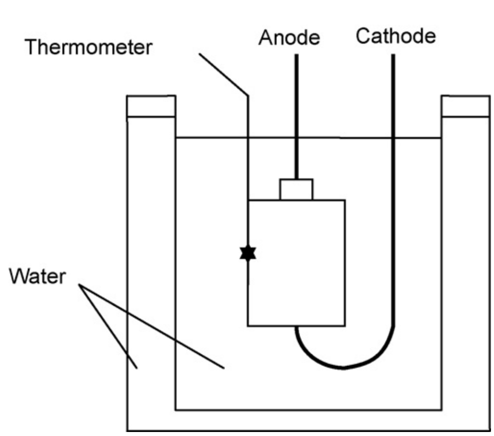

Fig. 1. Experiment device system. Each part of the device in which the tested battery is fixed is labeled.

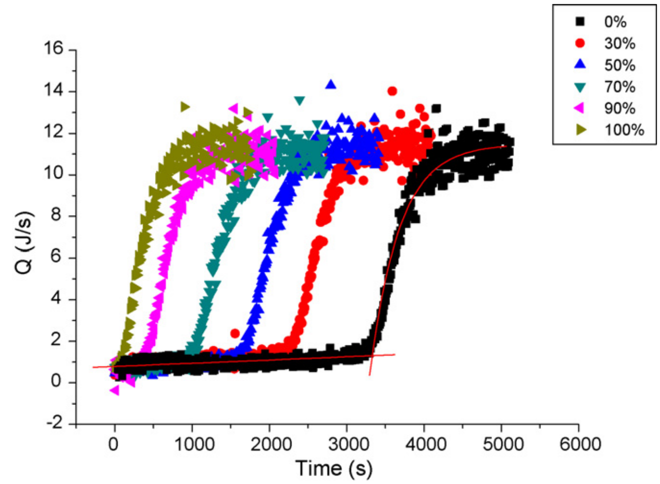

Fig. 2. Heat generation rate of 1C rate charge. Different curves from the right to the left denote SOC from 0 to 100%.

the charge process. Others can be obtained by linear transform.

Heat generation becomes more seriously when charge rate increases. One reason is that the amount of heat generated by side reaction in overcharging period remains nearly the same because of the same starting and finishing SOC while time is much shorter. Another reason is heat generated by electrical resistance becomes considerable when the current goes up, which is known as $P = I^2R$ (P denotes power, I denotes current and R denotes internal resistance).

Each curve is divided into two sections to help us understand what happens through the process:

(1) Normal charging section, heat generation rate is slowly increasing. According to Refs. [8–10], 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.
(2) Overcharge section, recombination whereby the generated oxygen and hydrogen return to water contributes to Q [10]:

$$2H + \frac{1}{2}O_2 \rightarrow H_2O, \quad -285.8\,\text{kJ mol}^{-1} \tag{2}$$

In 1C and 3C rate charge, heat generation rate increase asymptotically with charging time. In 5C rate charge, charge time was

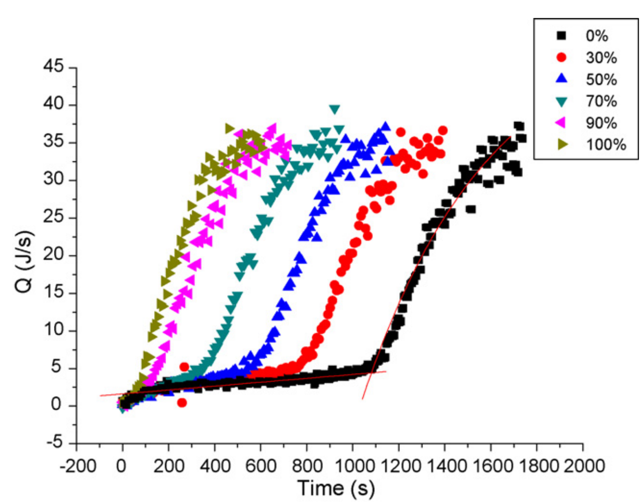

Fig. 3. Heat generation rate of 3C rate charge. Different curves from the right to the left denote SOC from 0 to 100%.

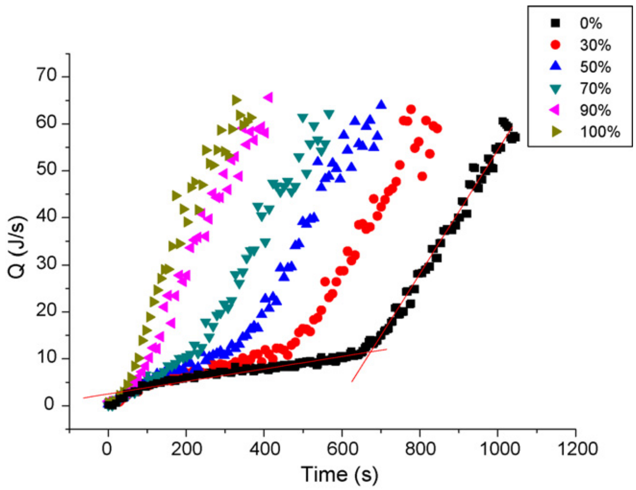

Fig. 4. Heat generation rate of 5C rate charge. Different curves from the right to the left denote SOC from 0 to 100%.

shorter and Q seems like a line.

Expressions of Q are

For 1C :

$$Q = \begin{cases} 0.74555 + 0.000158t & , t < 3303 \\ 11.50979 - 54303.77062 \times 0.99743^t & , 3303 < t < 5400 \end{cases} \quad (3)$$

For 3C :

$$Q = \begin{cases} 1.93313 + 0.00253t & , t < 1050 \\ 51.09361 - 329.78716 \times 0.9982^t & , 1050 < t < 1800 \end{cases} \quad (4)$$

$$\text{For } 5C: \quad Q = \begin{cases} 2.96826 + 0.01303t & , t < 653 \\ -75.54081 + 0.12909t & , 653 < t < 1080 \end{cases} \quad (5)$$

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

$$-\frac{dc}{dt} = kc \quad (6)$$

c denotes concentration of reactant.

For the reaction we presume reaction heat as ΔH (kJ mol^{-1}):

$$-\frac{d}{dt}\frac{d(\Delta H\, c)}{dt} = k\frac{d(\Delta H\, c)}{dt} \quad (7)$$

That is

$$-\frac{dQ}{dt} = kQ \quad (8)$$

and integral form is

$$Q = A - A\,e^{-kt} \quad (9)$$

where A is a constant.

As for side reaction mentioned above, expressions of Q for 1C and 3C rate charge in overcharge section can be written as

$$\text{For } 1C: \quad Q = 11.50979 - 54303.77062 \times 0.99743^t = 11.50979 - 11.50979 \times e^{-0.002573308(t-3287)} \quad (10)$$

$$\text{For } 3C: \quad Q = 51.09361 - 329.78716 \times 0.9982^t = 51.09361 - 51.09361 \times e^{-0.001801621(t-1035)} \quad (11)$$

The two equations 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.

Reaction inside the battery during 5C rate charge seems to be a zeroth order reaction. It may be caused by heat conductance and diffusion of reactants inside the battery, diffusion is the rate-determining step under high rate. And the heat conductivity limited much heat inside the battery. Therefore, heat generation rate may not help determine the reaction order of high rate charge because of the heat conductivity.

Quantities of heat generated in charge period are also measured by microcalorimeter, quantities of heat of 1C, 3C, and 5C rate charge are 18644.49, 24183.74, and 27176.76 J.

3.2. Thermal models

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

$$MC_p\frac{\partial T}{\partial t} = V\frac{1}{r}\frac{\partial}{\partial r}\left(k_r r\frac{\partial T}{\partial r}\right) + V\frac{\partial}{\partial z}\left(k_z\frac{\partial T}{\partial z}\right) + Q \quad (12)$$

$$\text{IC}: \quad T(r, z, 0) = T_0 \quad (13)$$

$$\text{BC}: \quad -k_r\left.\frac{\partial T}{\partial r}\right|_{r=R} = h(T|_{r=R} - T_\infty), -k_z\left.\frac{\partial T}{\partial z}\right|_{z=0,H} = h(T|_{z=0,H} - T_\infty) \quad (14)$$

C_p is average heat capacity, which is measured by microcalorimeter before charging 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; Q is heat generation rate, which is expressed by (3)–(5); h denotes heat transfer coefficient. Values are shown in Table 2.

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

$$\text{For } 1C: \quad T_\infty = 24.055 + 2.71373 \times \frac{t}{5400} \quad (15)$$

$$\text{For } 3C: \quad T_\infty = 24.055 + 2.88291 \times \frac{t}{1800} \quad (16)$$

$$\text{For } 5C: \quad T_\infty = 24.055 + 2.82556 \times \frac{t}{1080} \quad (17)$$

According to Newton's law of cooling:

$$Q = hA\,\Delta T \quad (18)$$

ΔT denotes temperature difference between battery wall and ambient temperature.

The experiment shows that ΔT is smaller than 3 °C, so we assume it to be constant for simplicity, 3 °C. Heat transfer coefficient is expressed by

$$h = \frac{Q}{A\,\Delta T} \quad (19)$$

Table 2
Values of parameters in thermal model

Parameters	Values
C_p, heat capacity (J kg^{-1} °C^{-1})	301.206
k_r, thermal conductivity in r-direction (J s^{-1} m^{-1} °C^{-1})	0.74[a]
k_z, thermal conductivity in z-direction (J s^{-1} m^{-1} °C^{-1})	0.85[a]
A, surface area (m^2)	0.00769
T_0, initial temperature (°C)	24.055

[a] Ref. [8].

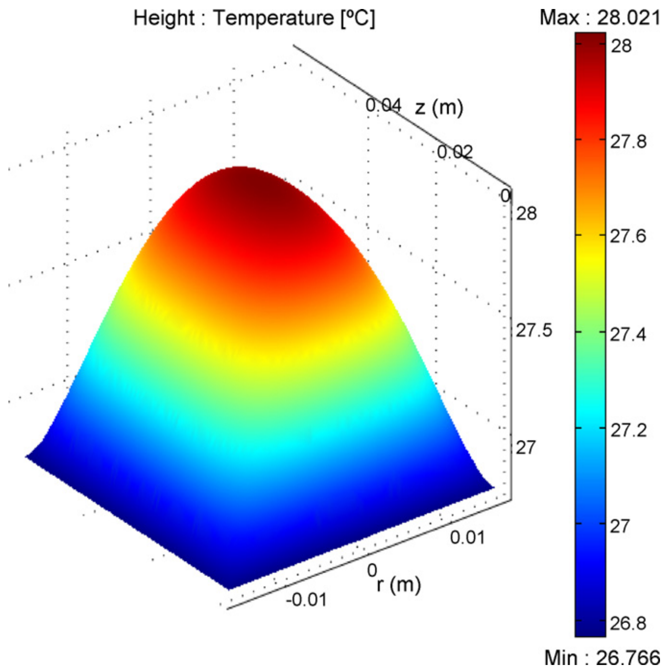

Fig. 5. Temperature distribution by calculation in tested battery after 1C rate charge. Red area has higher temperature than blue area. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Solutions of three equations are shown in Figs. 5–7, two-dimensional temperature profile in the *r*-direction and *z*-direction under at the end of 1C, 3C, and 5C rate charge. For batteries charged from SOC 0%, surface temperature of 3C rate charge is higher than the others, a possible reason is 3C rate charge generates more heat and there is enough time for heat to get outside of the battery. However, for batteries charged from SOC 100%, sur-

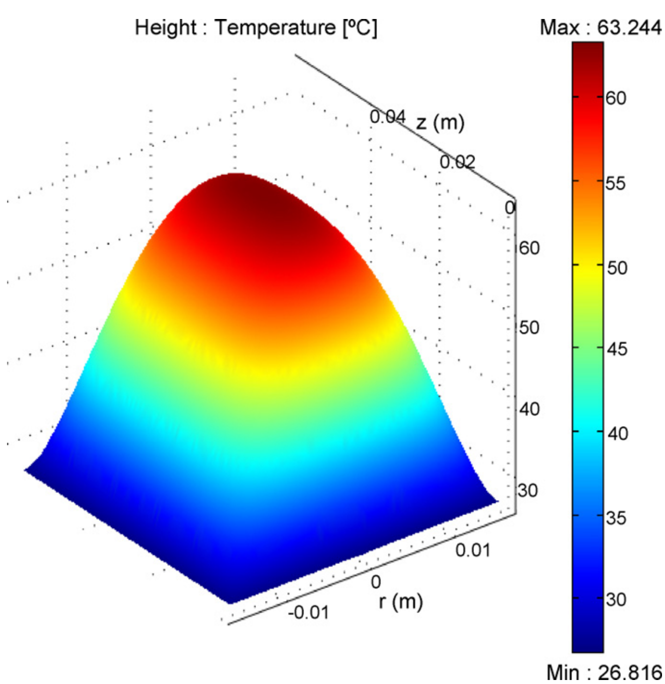

Fig. 6. Temperature distribution by calculation in tested battery after 3C rate charge. Red area has higher temperature than blue area. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

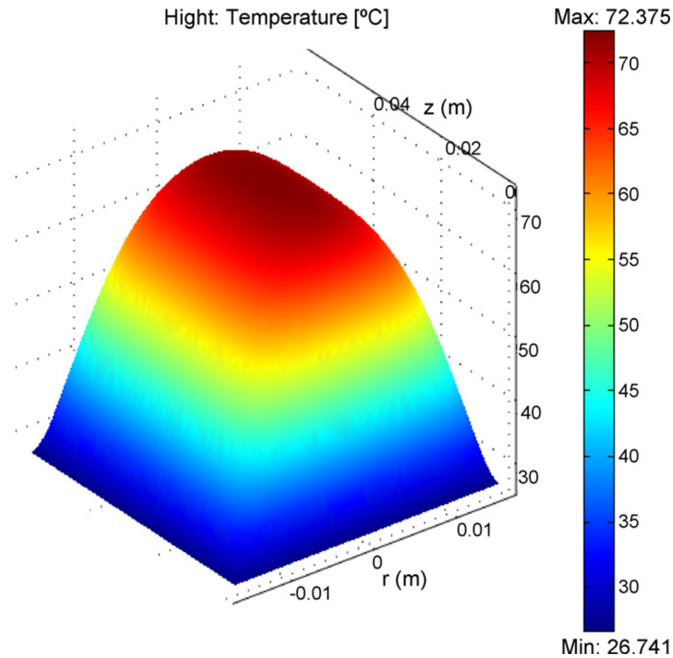

Fig. 7. Temperature distribution by calculation in tested battery after 5C rate charge. Red area has higher temperature than blue area. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

face temperature of 1C rate charge is higher because of longer time. The battery material cannot dissipate heat generated immediately under high rate charge owing to low heat conductivity. The inside temperatures of 3C and 5C rate charge are much higher than that of 1C rate charge, up to 63.24 and 72.38 °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 28.021 °C, the battery is under good working condition.

Surface temperature rises by calculation are 2.711, 2.761, and 2.686 °C. Comparing with the results of experiment, calculation results are lower than actual rises. It seems that we have overestimated the cooling efficiency possibly owing to estimation of *h*. The temperature rises are close especially for 1C and 3C rate charge as shown in Table 3, so we believe the model results are reliable.

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

Table 3
Comparison of experiment and calculation

Rate	Temperature	SOC					
		0%	30%	50%	70%	90%	100%
1C	Experiment	2.714	2.656	2.436	2.315	2.289	2.299
	Calculation	2.711	2.656	2.436	2.313	2.286	2.299
3C	Experiment	2.883	2.652	2.460	2.309	2.093	1.907
	Calculation	2.761	2.629	2.438	2.287	2.061	1.873
5C	Experiment	2.826	2.675	2.545	2.152	1.956	1.844
	Calculation	2.686	2.642	2.517	2.126	1.925	1.794

should be avoided in actual use. It may cause some damage to the battery.

3.3. Conclusions

We check the surface temperature of tested battery, calculation results are close to experiment results. The battery is overcharged to 150% of its actual capacity, temperature rise is about 3 °C. It is much lower than that under air-cooling condition.

There is still a problem that experiment results and calculation results do not match very exactly for 5*C* rate charge. The temperature rise is getting lower while heat generation of 5*C* rate charge is greater than 1*C* rate charge. A possible reason is that in the model 1*C* rate charge experiment takes more time so that heat generated by tested battery has enough to time get out, and the temperature falls down. As for 5*C* rate charge, time is much shorter and heat remained inside.

Acknowledgement

This work is supported by the National Key Basic Research and Development Program of China (Grant No. 2002CB211800).

References

[1] A.A. Pesaran, J. Power Sources 110 (2002) 377–382.
[2] M.S. Wu, Y.Y. Wang, C.C. Wan, J. Power Sources 74 (1998) 202–210.
[3] J. Harmel, D. Ohms, U. Guth, K. Wiesener, J. Power Sources 109 (2006) 88–93.
[4] B. Yann Liaw, K.P. Bethune, X. Guang Yang, J. Power Sources 110 (2002) 330–340.
[5] D. Bernadi, E. Pawlikowski, J. Newman, J. Electrochem. Soc. 132 (1985) 5–12.
[6] Y. Chen, J. Evans, Electrochim. Acta 39 (1994) 517–526.
[7] Y. Chen, J. Evans, J. Electrochem. Soc. 141 (1994) 2947–2955.
[8] J. Shi, F. Wu, S. Chen, C. Zhang, J. Power Sources 157 (2006) 592–599.
[9] N. Sato, J. Power Sources 99 (2001) 70–77.
[10] N. Sato, K. Yagi, JSAE Rev. 21 (2000) 205–211.
[11] M.-S. Wu, Y.-H. Hung, Y.-Y. Wang, C.-C. Wan, J. Electrochem. Soc. 147 (2000) 930–935.