Thermo-Electrochemical Study on the Heat Effects of LiFePO$_4$ Lithium-ion Battery During Charge-Discharge Process

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The heat effects of lithium-ion battery cathode could substantially affect the safety and attenuate lifetime of lithium-ion battery. In order to disclose the thermo-electrochemical behaviors of LiFePO$_4$ battery during charge-discharge process at various rates at $30\,^{\circ}\text{C}$, electrochemical-calorimetric measurements were employed in this study. The results showed that LiFePO$_4$ battery had a smaller polarization and a better reversibility at low rate (0.1C, 0.2C, 0.5C). With the increasing of the rate structure of cathode material LiFePO$_4$ was partially destroyed and impurities, like Li$_3$PO$_4$ and FeP$_2$, appeared at rate 1.0C and 2.0C. Formation of these impurities resulted in electrochemical performance deterioration of battery. The charge-discharge process of LiFePO$_4$ battery accompanied exothermic process and endothermic process at low rate (0.1C, 0.2C). When the rate increased to 1.0C, only exothermic phenomena existed. With the rate increasing heat production rate and the enthalpy change during charge-discharge process of LiFePO$_4$ battery increased. These suggest that appropriate rate for battery should be choose in order to avoid safety problem, which initiated by internal heat accumulation of battery.

1. INTRODUCTION

Lithium-ion batteries are key components of portable, entertainment, computing, and telecommunication equipment because of their high-energy storage density, high voltage, long cycle life, high-power sources, and ambient temperature operation. Although lithium-ion batteries have many attractive features, a few key issues have to be investigated for the practical applications of hybrid electrical vehicles (HEVs) with large capacity of energy storage. Heat control and management

is one of the most important issues in the lithium-ion batteries at high temperature or high charge/discharge rate will lower charge/discharge efficiency and lower the battery life, or even cause safety problem[1-5].

Olivine-type $LiFePO_4$ is regarded as the most promising alternative cathode material for Lithium-ion batteries because of its advantages of higher theoretic capacity (170 mAh·g^{-1}), lower cost, higher safety, and environmental friendliness. However, $LiFePO_4$ has low electronic and ion conductivities, low tap density, and poor low-temperature character. A large number of efforts have been made to overcome the electronic and ionic transport limitations by doping with super-valent cations, incorporating nanostructured designs, or coating electronically conductive agents. Much has been reported about the electrochemistry and structures of $LiFePO_4$ material[6-10], but little has been reported on such thermal behavior of this material as this paper. Understanding the thermal behavior of these heat generation sources would offer much valuable information to develop the battery thermal management strategies as well as cell design, optimization and operation. In the battery operation, the heat generation is mainly ascribed to the electrochemical reactions, the active polarization and the electric conductive resistance. In addition, high rates greatly increase the rate of heat generation in a battery. If the rate of heat generation is faster than heat dissipation, the battery temperature increases. This may bring the battery to a thermal runaway condition.

Calorimetry is an effective method to characterize the thermal behavior of batteries, various materials have been tested to evaluate their performance and to study their thermal behavior using electrochemical-calorimetric methods with commercial Li-ion cells[11-18]. However, researches are rarely focused on the point of analysis of thermodynamics parameters from button cells with microscale active material. These parameters from pocket-size cell are very important in optimizing battery design, fabrication, thermal management for the applications and model building through which the thermal characteristics of lithium-ion batteries can be studied conveniently.

In this paper, we focus the characterization of heat generation occurring during charge and discharge, especially cycling at various rates, by calorimetric measurement. And the emphasis of this is to analyze different heat generation sources a button cell.

2. EXPERIMENTAL

2.1. Materials

Commercially available $LiFePO_4$ powders and N-methyl-2-pyrrolidone (NMP) were provided by Hunan Shanshan Toda Advanced Material Co., Ltd. Acetylene black was obtained from ZhuHai TaiYi Battery Co., Ltd. Polyvinylidene fluoride (PVDF) was supported by Guangdong Jiejin Chemical Co., Ltd. All other chemicals were of analytical grade and the experimental water was grade II desalted water.

2.2. Battery preparation

Active material LiFePO$_4$ was mixed with acetylene black, PVDF binder (mass ratio of LiFePO$_4$, acetylene black and PVDF is 80:10:10) in NMP onto an aluminum foil current-collector. The electrodes were dried at 120℃ under vacuum for 6 h and pressed using a hydraulic press. CR2025 button cells were assembled using lithium metal foil as anode and the above prepared electrode as cathodes, Celgard 2300 microporous membrane was used as separator. LiPF$_6$ (1.0M) in a 1:1:1 (v/v/v) mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethylmethyl carbonate (EMC) was used as electrolyte. The cells were assembled in an argon-filled glove box.

2.3. Electrochemical-calorimetric measurements

The electrochemical and thermodynamic properties of LiFePO$_4$ were measured by using CR2025 button cell. Charge-discharge performances were evaluated using a Land automatic battery test system (CT2001A, China). The charge/discharge voltage region was 2.2-3.8V, and the current was 0.1C, 0.2C, 0.5C, 1.0C and 2.0C rate. Heat generation occurring during charge and discharge was recorded by an eight-channel micro-calorimeter (3114/3236 TAM Air, Swiss). The calorimeter was electrical calibrated at 303.15K before experiment. As shown in Fig. 1, LiFePO$_4$/Li CR2025 button cell was put into the ampoule bottle, which was hanging up in the channel of micro-calorimeter. The calorimeter was then stabilized at constant temperature (303.15K) for 12 h. The positive and negative terminals of the button cell were connected to the external Land automatic battery test system with the aid of 2 copper wires, and then the charge/discharge studies at 0.1C, 0.2C, 0.5C, 1.0C and 2.0C rate were carried out. The thermal spectra were recorded after electrode reaction started.
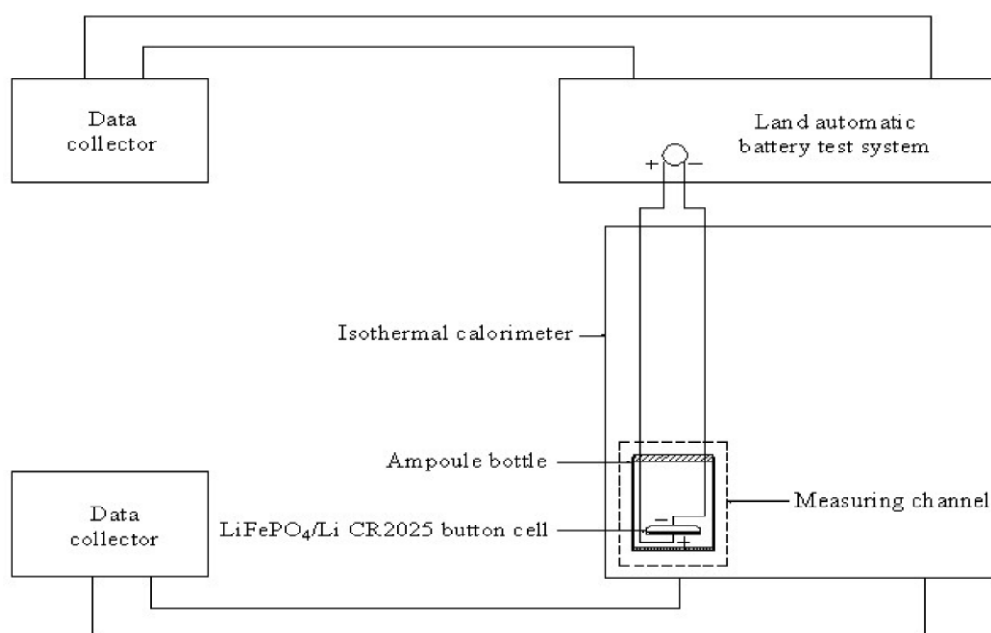

Figure 1. Schematic draw of electrochemical-calorimetric measurement device

2.4. Structure analysis

The button cell was disassembled after the electrochemical-calorimetric experiment. The powder X-ray diffraction (XRD, Rint-2000, Rigaku) measurement (Cu K_α radiation with a step time of 2^0 min^{-1}) was carried out to identify the crystalline phase of LiFePO$_4$.

3. RESULTS AND DISCUSSION

3.1. Electrochemical performances of LiFePO$_4$

The initial charge-discharge curves of LiFePO$_4$ at different charge-discharge rate are shown in Fig. 2. It can be shown from Fig. 2 that the lower rate, the greater charge-discharge capacity, the flatter charge-discharge platform, and the smaller voltage difference between the charge platform and discharge platform. Therefore, the battery had a smaller polarization and a better reversibility during low range charging and discharging process. Structure and morphology of cathode material was partially destroyed in the charge-discharge process with high current density. So with the increasing of charge-discharge rates, charge-discharge capacity of battery reduced. For example, the discharge capacity of LiFePO$_4$ at 0.1C rate is 151.3mAh g^{-1}, and at 2.0C rate is 144.5 mAh g^{-1}.
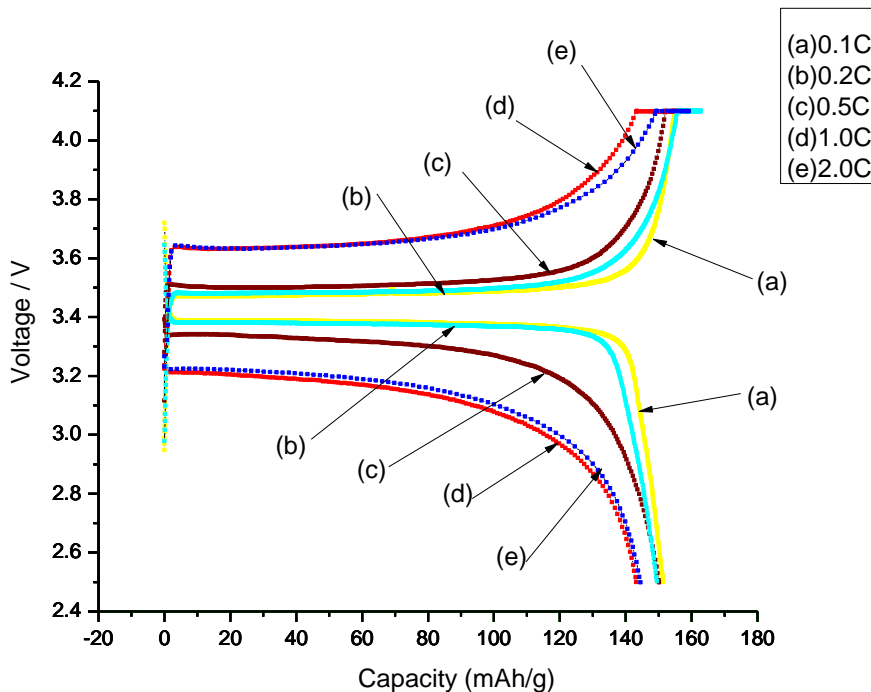

Figure 2. The rate capacity of LiFePO$_4$

In order to verify above analysis results, the crystalline nature of the cathode material LiFePO$_4$ during cycling at different charge-discharge rates was identified with X-ray diffraction (XRD). Fig. 3

shows the X-ray diffraction (XRD) patterns of the cathode material LiFePO$_4$ at different charge-discharge rates. All the diffraction peaks deflected to high angle, the relative peak areas and intensities ascended slightly on increasing charge-discharge rates, most of which is 0.5C. These facts elucidate crystalline phase content of the cathode material LiFePO4 was increased. With the increasing of charge-discharge rates 3 new diffraction peaks was observed in the XRD pattern at 1.0C and 2.0C.These diffraction peaks belong to respectively Li$_3$PO$_4$ phase, Fe$_2$O$_3$ phase and FeP$_2$ phase by indexing PDF card. In charge process, part of Fe^{3+} ions formed Fe$_2$O$_3$ compound, and iron deficiency in crystal lattice LiFePO$_4$ might result in some Fe^{2+} sites were occupied by other ions, and impurities, like Li$_3$PO$_4$ and FeP$_2$, appeared. Formation of these impurities will result in electrochemical performance deterioration of the cathode materials.
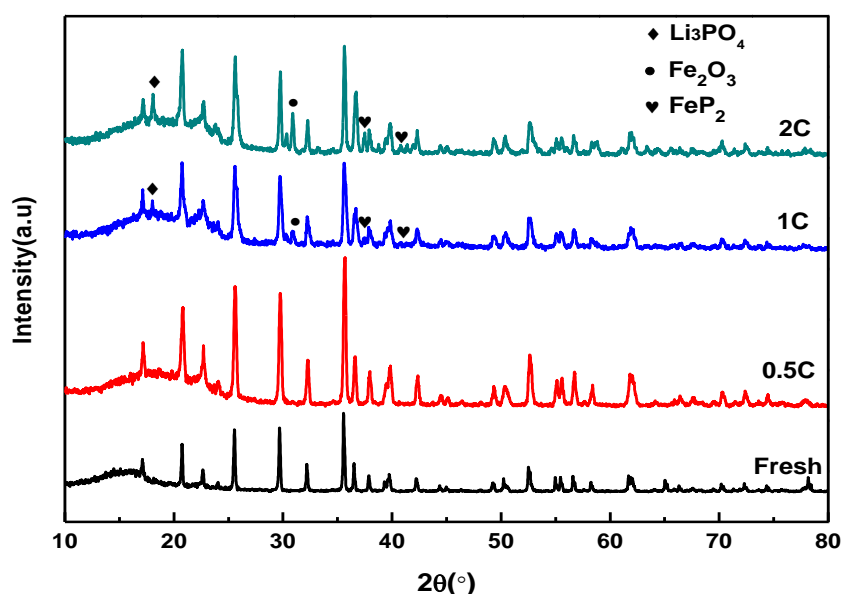

Figure 3. The XRD patterns of the cathode material LiFePO$_4$ before and after cycling

3.2. Thermal behaviors of LiFePO$_4$

Fig. 4 shows the variation in the heat flow of LiFePO$_4$ battery, as a function of time at different charge-discharge rates (0.1C, 0.2C, 0.5C, 1.0C, 2.0C). It can be shown from Fig. 4 that two obvious exothermic peaks appeared at all the curves of heat flow and voltage of LiFePO$_4$ with time at different charge-discharge rates. The heat flow slowly increased at the initial stage of charge-discharge process at 0.1C and 0.2C rate, but increased rapidly at 0.5C, 1.0C and 0.2C rate. With the increasing of the rate, the heat flow increased during the charge-discharge process, and that's because irreversible heat production rate of the battery increased with the increasing of the charge-discharge rate[19]. The whole charge-discharge stage of LiFePO$_4$ battery accompanied exothermic process and endothermic process at 0.1C and 0.2C rate. It follows that exothermic and endothermic phenomena of the battery will be determined together by reversible heat and irreversible heat. When the rate increased to 1.0C, only exothermic phenomena existed in the whole charge-discharge process of battery. Because irreversible

heat played a dominant part in the charge-discharge process when its' current was large. Heat effect during charge-discharge process of battery came mainly from irreversible heat, which produced by overcoming battery internal resistance. When the battery was in maximum discharge degree, great irreversible heat produced due to the electrodes reached at serious polarization state. Irreversible heat showed an exothermic effect no matter the charge process or the discharge process.
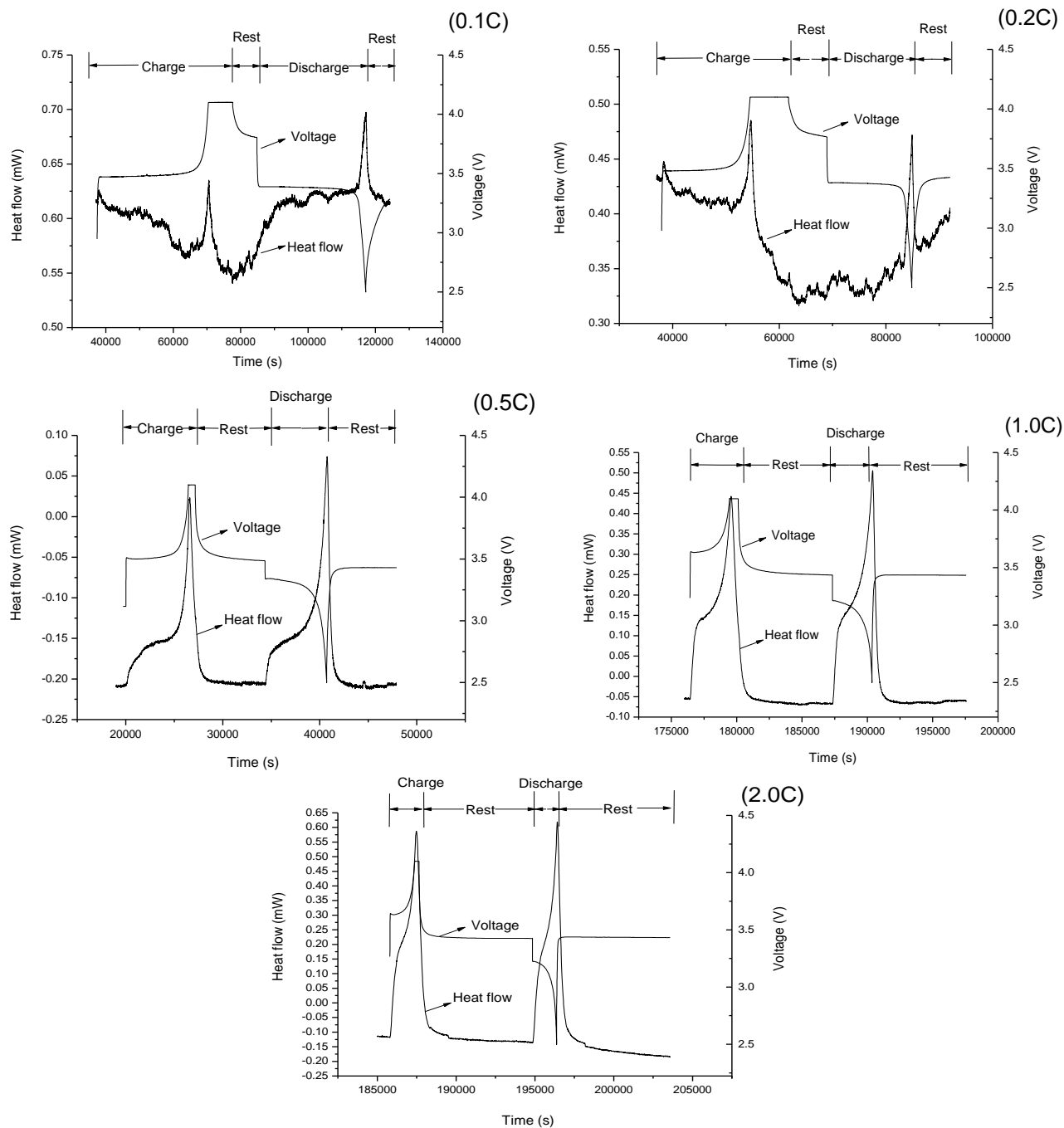

Figure 4. Change curves of heat flow and voltage of $LiFePO_4$ with time at different charge-discharge rates

The Enthalpy change for LiFePO$_4$ at various charge-discharge rates (0.1C, 0.2C, 0.5C, 1,0C and 2.0C) are shown in Fig. 5. Heat production rate was linearly related to the rate, and decreased with the rate decreasing. The smaller the rate, the less the total heat production rate, the less the total enthalpy change in the reaction and the higher the safety performance of the battery.
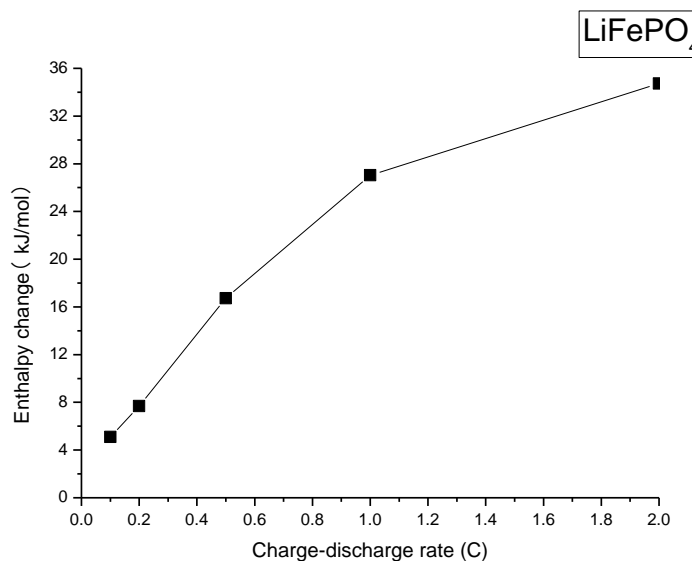

Figure 5. Enthalpy change against charge-discharge rate of LiFePO$_4$

The enthalpy charge ($\triangle$H) was calculated by the following equation:

$$q_{\text{total}} = q_{ch} + q_{disch} = \int h(t)dt \qquad (1)$$

$$n = \frac{Q}{F} = \frac{\int i(t)dt}{F} \qquad (2)$$

$$\Delta H = \Delta H_{ch} + \Delta H_{disch} = q_{\text{total}} / n \qquad (3)$$

where q_{total} is total heat production rate in the reaction, $h(t)$ is the heat flow at time t, n is the number of electrons passed in the reaction, Q is quantity of electricity in the reaction, F is the Faraday's constant, and $i(t)$ is the current at time t. Table 1 summarizes detailed information about heat generations for LiFePO$_4$/Li CR2025 button cell.

The data listed in Table 1 show that exothermic phenomenon played a dominant role in total heat effects during the charge-discharge process of the battery. With the rate increasing, the enthalpy change (ΔH) in the reaction increased from 5.100 kJ·mol^{-1} (0.1C) to 34.731 kJ·mol^{-1} (2.0C). Heat production rate during the charge-discharge process of battery increased with the rate increasing. The reason is that with the rate increasing, current increased, battery polarization effect increased, and quantity of heat increased. The same results were received by studying the thermal behaviors of

$LiNi_{0.8}Co_{0.2}O_2$ at different current levels[20]. Heat production rate of battery during the charge and discharge process at 2.0C were 815.161 mW·s, 824.476 mW·s, respectively (Table. 1), and at 0.1C were 305.632 mW·s, 111.524 mW·s, respectively.

Table 1. Heat generation parameters for $LiFePO_4$/Li CR2025 button cell

Rate	q_{ch} (mW·s)	q_{disch} (mW·s)	q_{total} (mW·s)	Q (C)	$n \times 10^5$ (mol)	ΔH_{ch} (kJ·mol^{-1})	ΔH_{disch} (kJ·mol^{-1})	ΔH (kJ·mol^{-1})
0.1C	-305.632	-111.524	-417.156	7.892	8.179	-2.296	-2.804	-5.100
0.2C	-344.543	-193.615	-538.158	6.753	6.999	-1.911	-5.778	-7.689
0.5C	-496.809	-609.307	-1106.116	6.384	6.616	2.139	-18.858	-16.719
1.0C	-986.232	-964.530	-1950.762	6.960	7.212	-0.107	-26.942	-27.049
2.0C	-815.161	-824.476	-1639.637	4.555	4.721	0.293	-35.024	-34.731

*where the footnotes ch and disch correspond to the charge and discharge processes, respectively.

4. CONCLUSIONS

The thermal stability of cathode materials plays a key role in lithium-ion battery safety, and the electrochemical-calorimetric measurements show good performance in studying the thermo-electrochemical behaviors of $LiFePO_4$.

(1) The lower rate, the greater charge-discharge capacity, the flatter charge-discharge platform, and the smaller voltage difference between the charge platform and discharge platform. Therefore, the $LiFePO_4$ battery had a smaller polarization and a better reversibility at low rate. With the increasing of the rate structure of cathode material $LiFePO_4$ was partially destroyed, electrochemical performance deteriorated.

(2) The whole charge-discharge stage of $LiFePO_4$ battery accompanied exothermic process and endothermic process at low charge-discharge rate (0.1C, 0.2C). When the rate increased to 1.0C, only exothermic phenomena existed. With the rate increasing heat production rate and the enthalpy change during the charge-discharge process of $LiFePO_4$ battery increased.

Based on the experiment results obtained in this article, we could conclude that appropriate charge-discharge rate for battery should be choose in order to avoid safety problem, which initiated by internal heat accumulation of battery.

References

1. G. W. Ling, X. P. Zhu, Y. B. He, Q. S. Song, B. H. Li, Y. J. Li, Q. H. Yang, Z. Y. Tang, *Int. J. Electrochem. Sci.* 7 (2012) 2455.
2. H. B. Rem, X. Y. Liu, H. P. Zhao, Z. H. Peng, Y. H. Zhou, *Int. J. Electrochem. Sci.* 6 (2011) 727.
3. Z. Zhang, D. Fouchard, J. R. Rea, *J. Power Sources* 70 (1998) 16.
4. N. Sato, *J. Power Sources* 99 (2001) 70.
5. S. C. Chen, C. C. Wan, Y. Y. Wang, *J. Power Sources* 140 (2005) 111.
6. S. Franger, F. L. Cras, C. Bourbon, H. Rouault, *J. Power Sources* 199 (2003) 252.
7. R. Dominko, M. Bele, M. Gaberscek, M. Remskar, D. Hanzel, S. Pejovnikand, J. Jamnik, *J. Electrochem. Soc.* 152 (2005) 607.
8. D. H. Kim, J. Kim, *J. Phys. Chem. Solids* 68 (2007) 734.
9. J. Gao, J. J. Li, X. M. He, C. Y. Jiang, C. R. Wan, *Int. J. Electrochem. Sci.* 6 (2011) 2818.
10. H. C. Wong, J. R. Carey, J. S. Chen, *Int. J. Electrochem. Sci.* 5 (2010) 1090.
11. X. W. Zhang, *J. Electrochim. Acta* 56 (2011) 1246.
12. H. F. Jin, Z. Liu, *J. Power Sources* 189 (2009) 445.
13. K. Onda, T. Ohshima, *J. Power Sources* 158 (2006) 535.
14. Y. Saito, *J. Power Sources* 146 (2005) 770.
15. S. A. Hallaj, J. Prakash, J. R. Selman, *J. Power Sources* 87 (2000) 186.
16. Z. Y. Jiang, J. Zhang, L. J. Dong, J. H. Zhuang, *J. Electroanal. Chem.* 469 (1999) 1.
17. J. S. Hong, H. Maleki, S. A. Hallaj, L. Redey, J. R. Selman. *J. Electrochem. Soc.* 145 (1998) 1489.
18. Y. Kobayashi, H. Miyashiro, K. Kumai, K. Takei, T. Iwahori, I. Uchida. *J. Electrochem. Soc.* 149 (2002) 978.
19. V. Vilayanurras, Viswanathan, D. W. Choi, D. H. Wang W. Xu, T. Silas, R. E. Williford, J. G. Zhang, J. Liu, Z. G. Yang, *J. Power Sources* 195 (2010) 3720.
20. W. Q. Lu, H. Yang, J. Prakash, *J. Electrochim. Acta* 51 (2006) 1322.