

## Assessment of Thermo-electrochemical Performance on Cathode Materials for Lithium Ion Cells

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In this paper, we adopted electrochemical-calorimetric method to study the heat production of lithium ion batteries in which  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  acted as cathode materials at a constant ambient temperature (313.15 K) during different charge-discharge processes. And the results of thermo-electrochemical properties on  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  cathode materials have been compared to the results on  $\text{LiFePO}_4$  and  $\text{LiMn}_2\text{O}_4$  materials from our previous studies [1,2]. By comparing results of different electrode materials, we concluded that charge-discharge rate was one of the key factors affecting the lithium-ion batteries. With the increasing of rate, heat production and enthalpy change of different cathode materials increased and discharge capacity decreased. The greater the entropy value was, the greater the confusion degree and reversible worse were. At low rate (0.2 C) entropy value of  $\text{LiFePO}_4$  was the largest, followed by  $\text{LiMn}_2\text{O}_4$  and  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ . Cycle performance of  $\text{LiFePO}_4$  was the worst, which was consistent with electrochemical performance analysis. These results provide a theoretical basis for optimizing design of the battery structure and reveal that the choosing of suitable charge-discharge rate is critical to the thermal management.

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**Keywords:** assessment, lithium ion cell, thermo-electrochemistry, cathode material, electrochemical-calorimetry

### 1. INTRODUCTION

In 1992,  $\text{LiCoO}_2$  battery advent of SONY has been widely used in some electronic devices, which greatly promoted the development of lithium ion batteries [3-5]. In recent years, the application

of lithium ion battery in the field of military and aerospace increased gradually, and moving towards to energy storage, electric vehicles and other fields, which promoted development of lithium ion battery [6-8]. Lithium-ion batteries benefit mankind, meanwhile, their safety issues have been exposed. A series of chemical reactions accompanied by a large of heat occurred in the battery during charge and discharge process, especially at high rate charge-discharge or high environment temperature [9,10]. If the heat could not be dissipated in time, it may cause thermal runaway, such as smoking, fire and even explosion, thereby endangering personal and property safety [11-13]. It is necessary to analyze the thermal effects of the battery.

At present, our research group has carried out thermo-electrochemical properties directing at  $\text{LiFePO}_4$  and  $\text{LiMn}_2\text{O}_4$  cathode material during charge-discharge process at different ambient temperatures and has made some progress [1,2]. However, spinel  $\text{LiMn}_2\text{O}_4$  and olivine-type  $\text{LiFePO}_4$  are difficult to meet the requirements of high specific capacity and high energy density. Therefore, people start working on high capacity cathode material. Nickel rich layered nickel cobalt manganese oxide composite materials (such as  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ ,  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ ) because of the high discharge capacity about  $200 \text{ mAh g}^{-1}$  have been considered to be one of the most potential cathode materials in the future and have been used as the key energy storage materials in electric vehicles [14-16]. Cathode materials of lithium-ion batteries have pivotal roles in their safeties. Performance of cathode material and its assessment method received much concern. At present, domestic and foreign scholars for cathode materials research focuses on characterizing the morphology of material structure and assessing electrochemical performance [17-20], but the thermodynamic parameters of the battery system (enthalpy variation  $\Delta_r H_m$ , entropy change  $\Delta_r S_m$  and Gibbs free energy change  $\Delta_r G_m$ ) have been carried out relatively less [21-23]. It is more reasonable that comparing the electrochemical properties and thermodynamic properties of the batteries comprehensively than those obtained by the conventional electrochemical method. Thus the thermal safety of lithium ion batteries could be predicted, providing a comprehensive assessment of the positive electrode materials, helping to optimize the design of the cell structure and thermal management systems. It will help to assess the positive material and solve the problem of heat dissipation interior of the battery.

Based on the above analysis, we studied various cathode materials ( $\text{LiFePO}_4$ 、 $\text{LiMn}_2\text{O}_4$ 、 $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ ) batteries in different charge and discharge rates by using of Air TAM isothermal calorimeter and LAND battery testing system coupling technique to obtain thermal and chemical parameters which were combined with the electrochemical performance to reveal the effect rules of cells and establish an assessing method based on electrochemical-calorimetric technique in this paper.

## 2. EXPERIMENTAL

### 2.1. Preparation of $\text{LiNi}_{0.5}\text{Mn}_{0.2}\text{Co}_{0.3}\text{O}_2$ cathode material

The prepared  $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$  precursor powder (Gold Shine Energy Materials Co.,Ltd) was mixed with  $\text{Li}_2\text{CO}_3$  with a molar ratio of (Li:M=1.05:1, M=Ni,Co,Mn) manual grinding about 40

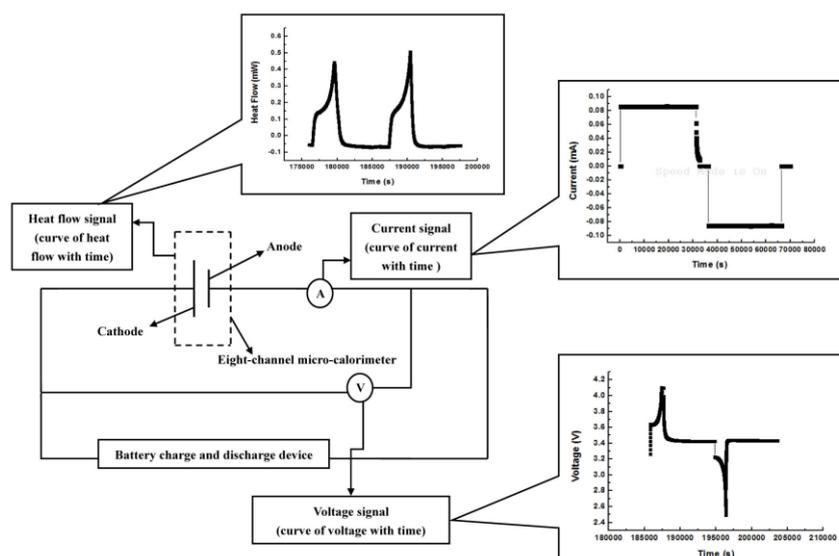
min and was first calcined at 500 °C for 5 hrs in air then heated to 960 °C for 10 hrs in air with heating rate of 5 °C min<sup>-1</sup> and cooling of the sample to obtain LiNi<sub>0.5</sub>Mn<sub>0.2</sub>Co<sub>0.3</sub>O<sub>2</sub> cathode material.

## 2.2. Fabrication of the CR2025 button cells

The LiNi<sub>0.5</sub>Mn<sub>0.2</sub>Co<sub>0.3</sub>O<sub>2</sub> cathode slurry was prepared by mixing the acetylene black, poly vinylidene fluoride (PVDF) binder in a weight ratio of 8:1:1 dissolved in N-methyl-2-pyrrolidone (NMP). The slurry was coated onto aluminum foil current collector and dried overnight at 393.15 K in a vacuum oven, then punched and weighed. The CR2025 button cells were assembled in a glove box filled with argon using Li metal as the anode, while the electrolyte solution was 1.0 mol L<sup>-1</sup> LiPF<sub>6</sub> in ethylene carbonate(EC)/dimethyl carbonate/(DMC)/ethylmethyl carbonate(EMC) (v:v:v, 1:1:1) and Celgard 2300 microporous membrane were acted as a separator.

## 2.3. Thermo-electrochemical performance test

Research idea of electrochemical-calorimetric measurement device is shown in Fig. 1. The CR2025 type cells were put in the bottom of closely fitted glass ampule bottles, which suspended in the channels of an eight-channel microcalorimeter (3114/3236 TAM Air, Sweden). The positive and negative electrodes of the cells were connected with Land Automatic Battery Test System (CT2001A, China) by copper wires. Heat flow of batteries at 313.15 K was measured during different charge-discharge rates (0.2 C, 0.5 C, 1.0 C) setting voltage range of 2.7-4.6 V. Cyclic voltammetry test of LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> battery was carried out at a scan rate of 0.1 mV s<sup>-1</sup> in the voltage range of 2.7-4.8 V using CHI 760 electrochemical workstation (Shanghai Chen Hua Instrument Co., Ltd).

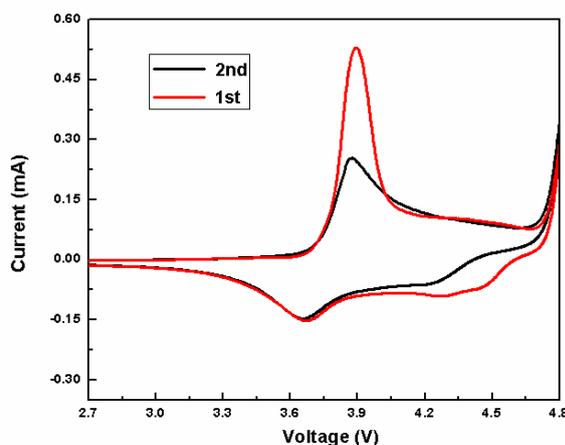


**Figure 1.** Schematic diagram of thermo-electrochemical study on lithium ion cell [2] (L. B. Song, Z. L. Xiao, L. J. Li, Q. Q. Zhou, *J. Solid. State Electrochem.*, 19 (2015) 2167. With permission of Springer).

### 3. RESULTS AND DISCUSSION

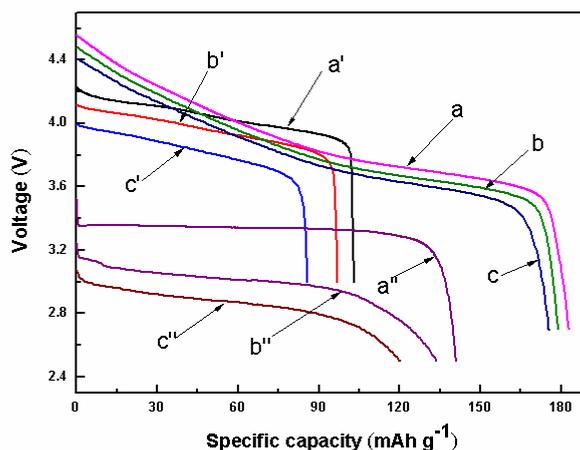
#### 3.1. Electrochemical performance

Cyclic voltammetry (CV) is a useful technique to evaluate the electrochemical performance of the electrode material. The CV curves for  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  cell are shown in Fig. 2. The figure showed that two oxidation peaks were near 3.91 V and 4.43 V corresponding to the  $\text{Ni}^{2+}/\text{Ni}^{3+}$  and  $\text{Co}^{3+}/\text{Co}^{4+}$ , while the reduction peaks appeared in the 3.67 V and 4.43 V in the first cycle. This is similar to the result of Zhu et al [24], but the result of Yang et al [25] is differ: the anodic peak in first cycle occurred at 4.22 V, whereas the main cathodic peak was located at 3.60 V. With the increase of the number of cycles, the current density of oxidation peak decreased. The change of current density was most obvious in which the oxidation peak shifted to a lower voltage (about 3.87 V), but reduction peak position almost had no changes and the current density decreased, which indicated the first cycle belonged to the activation process of electrode. The greater electric potential difference was, the greater electrode polarization was. The shift of oxidation peak during the cycle led to polarization increase, so that the discharge capacity decayed gradually, which was consistent with the results of cycle ability.



**Figure 2.** Cyclic voltammetry of the  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  /Li cathode between 2.7 and 4.8 V at a scan rate of  $0.1 \text{ mV s}^{-1}$ .

The curves of initial discharge under different rates for batteries with different positive materials are shown in Fig. 3. It could be known from Fig. 3 that with the increase of discharge rates, the discharge capacity decreased and the voltage of the platform decreased. With the increase of the discharge rates, the current increased, the irreversible polarization of the electrode material increased, the structure and microstructure of the electrode material were damaged, which led to the decrease of the battery capacity. The first discharge capacities of various batteries at different rates are shown in Table 1. The discharge capacity of  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  at different rates was the highest, and the discharge capacity was  $182.4 \text{ mAh g}^{-1}$  at 0.2 C. The discharge capacity of  $\text{LiMn}_2\text{O}_4$  was the lowest, and the discharge capacity was  $89.7 \text{ mAh g}^{-1}$ .



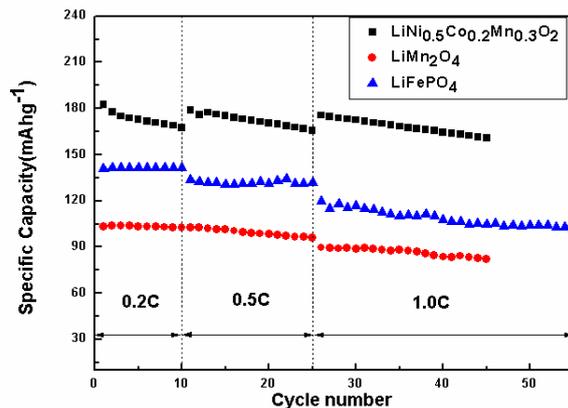
**Figure 3.** Discharge curves of lithium ion cells: 0.2 C (a); 0.5 C (b); 1.0 C (c) ( $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ ); 0.2 C (a'); 0.5 C (b'); 1.0 C (c') ( $\text{LiMn}_2\text{O}_4$ ) [2] (L. B. Song, Z. L. Xiao, L. J. Li, Q. Q. Zhou, *J. Solid. State Electrochem.*, 19 (2015) 2167. With permission of Springer) and 0.2 C (a''); 0.5 C (b''); 1.0 C (c'') ( $\text{LiFePO}_4$ ) [2] (L. B. Song, Z. L. Xiao, L. J. Li, Q. Q. Zhou, *J. Solid. State Electrochem.*, 19 (2015) 2167. With permission of Springer).

**Table 1.** Discharge performance of lithium ion cells at 313.15 K.

Samples	Initial discharge capacity ( $\text{mAh g}^{-1}$ )		
	0.2 C	0.5 C	1.0 C
$\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$	182.4	178.8	175.5
$\text{LiMn}_2\text{O}_4^{\text{a}}$	103.1	102.8	89.7
$\text{LiFePO}_4^{\text{b}}$	141.0	133.8	119.9

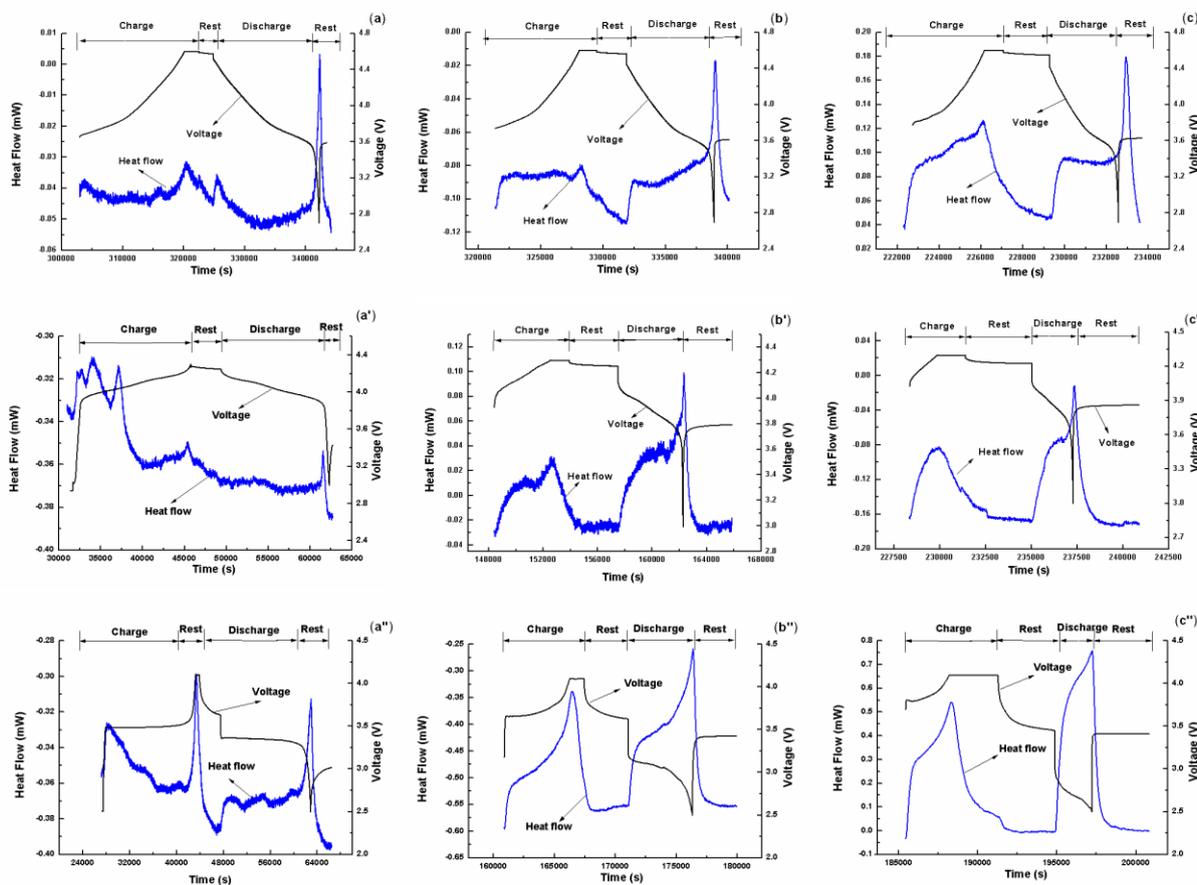
<sup>a,b</sup> Initial discharge capacity were come from the reference [2] (L. B. Song, Z. L. Xiao, L. J. Li, Q. Q. Zhou, *J. Solid. State Electrochem.*, 19 (2015) 2167).

Fig. 4 shows the curves of cycling performance of lithium ion cells with different positive materials at 313.15 K. It could be known that the discharge rate had a certain influence on the cycling performance of batteries. As the discharge rate increased, discharge capacity of batteries decreased gradually. The possible reason was that the higher the rate was, the higher the discharge current and the more irreversible polarization of the battery were. Cycle stability of  $\text{LiMn}_2\text{O}_4$  battery was the best. The discharge capacity had almost no change at low rate (0.2 C). And capacity fading was slower than other batteries at high rate (1.0 C). However, the discharge capacity of  $\text{LiMn}_2\text{O}_4$  was the lowest, and the discharge capacity was only half that of  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  battery at 0.2 C.



**Figure 4.** Cycle ability performance of lithium ion cells at 313.15 K [2] (L. B. Song, Z. L. Xiao, L. J. Li, Q. Q. Zhou, *J. Solid. State Electrochem.*, 19 (2015) 2167. With permission of Springer).

3.2. Electrochemical performance



**Figure 5.** Change curves of heat flow and voltage of lithium ion cells with time at different charge-discharge rates at 313.15 K: 0.2 C (a); 0.5 C (b); 1.0 C (c) ( $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ ); 0.2 C (a'); 0.5 C (b'); 1.0 C (c') ( $\text{LiMn}_2\text{O}_4$ ) [2] (L. B. Song, Z. L. Xiao, L. J. Li, Q. Q. Zhou, *J. Solid. State Electrochem.*, 19 (2015) 2167. With permission of Springer) and 0.2 C (a''); 0.5 C (b''); 1.0 C (c'') ( $\text{LiFePO}_4$ ) [2] (L. B. Song, Z. L. Xiao, L. J. Li, Q. Q. Zhou, *J. Solid. State Electrochem.*, 19 (2015) 2167. With permission of Springer).

Heat flow curves of various batteries during the initial charge-discharge process with different rates (0.2 C, 0.5 C, 1.0 C) at 313.15 K are shown in Fig. 5. From the graphs we knew that all curves had obvious exothermic peaks in the process of charging and discharging. At high rates (0.5 C, 1.0 C), heat flow curves existed two sharp exothermic peaks in the charge stage and discharge stage. At low rate (0.2 C) the  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  battery had many relatively flat peaks in the heat flow curve. The initial stage of charging was a relatively small exothermic peak. In the late period (3.6 V), the exothermic effect increased rapidly. At higher rate (0.5 C, 1.0 C) the initial discharge (4.6 V) increased rapidly.

The thermal effect of the battery includes two parts during charge-discharge process: reversible (reaction heat) and irreversible heat (polarization heat, Joule heat) [21,26]. The polarization of battery is little at low charge discharge rate and polarization heat is little [27]. Therefore exothermic peaks in the heat flow curve were mainly derived from the reaction heat of the battery at low rate. On the basis of CV result, 3.7-4.0 V and near 4.4 V represent the oxidation process, while 3.5-3.8 V and 4.2-4.5 V are the reduction process. Shaju et al [28] concluded that redox process at 3.6-3.8 V corresponded to  $\text{Ni}^{2+}/\text{Ni}^{4+}$  and that at 4.55-4.65 V to the  $\text{Co}^{3+}/\text{Co}^{4+}$  couple. At high rate, the polarization of the battery was large, and the polarization heat was high, so polarization heat was superimposed with the heat generated by the reaction heat. This was why we could not see obvious reaction heat peak. We are doing further research to explain this phenomenon perfectly.

According to voltage, current, time and corresponding heat flow data of charging and discharging process, we obtained heat production and quantity of electricity by integrating heat flow-time curve and current-time curve during the charging and discharging process of the battery. At low rate (0.2 C) charge discharge, the current density was lower. We found that irreversible heat of the charge and discharge process was approximately equal, and the absolute value of reversible heat was equal to each other [29]. At constant temperature and constant press, the amount of substance( $n$ ), enthalpy change( $\Delta_r H_m$ ), entropy change( $\Delta_r S_m$ ) and Gibbs free energy change( $\Delta_r G_m$ ) for the chemical reaction can be calculated using the following formulas:

$$n = Q / F \quad (1)$$

$$\Delta_r H_m = q / n \quad (2)$$

$$\Delta_r S_m = -(q_{ch} - q_{disch}) / 2nT \quad (3)$$

$$q_r = -T\Delta_r S_m \quad (4)$$

$$\Delta_r G_m = \Delta_r H_m - T\Delta_r S_m \quad (5)$$

Where  $Q(C)$  is the quantity of electricity in the reaction.  $F(C \text{ mol}^{-1})$  is the Faradic constant.  $q(mJ)$  is the total heat,  $q_{ch}(mJ)$  and  $q_{disch}(mJ)$  are the heat of charge and discharge, respectively.  $q_r(mJ)$  is Peltier heat, which produced in the reversible reaction.  $T(K)$  is the operation temperature.

Thermodynamic parameters of various batteries with different rates (0.2 C, 0.5 C, 1.0 C) at 313.15 K were obtained (Table 2). With the increase of charge and discharge rates, heat generation of the battery during charge discharge process increased. The possible reason was that with the charge discharge rate increasing, the charge discharge current increased, the battery polarization effect was enhanced and the heat generation increased. The irreversible heat contains the polarization heat and the Joule heat, which increases with the current density. As can be seen from table 2, the enthalpy change

value  $\Delta_r H_m$  of different positive electrode material batteries during charge and discharge cycle increased with the increasing of the rates. At 1 C, enthalpy change of LiFePO<sub>4</sub> battery was about 3 times of LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> battery, and 2.37 times of LiMn<sub>2</sub>O<sub>4</sub> battery. It is well known that  $\Delta_r S_m$  value is greater, the confusion degree greater, reversible worse and capacity fading faster. The  $\Delta_r S_m$  values of LiFePO<sub>4</sub> battery, LiMn<sub>2</sub>O<sub>4</sub> battery, and LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> cell were 276.8, 1.761, 1.728 J mol<sup>-1</sup> K<sup>-1</sup>. It was found that the reversibility of LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> was the best and LiFePO<sub>4</sub> was the worst, which was consistent with the results of the electrochemical performance.

**Table 2.**  $\Delta_r H_m$ ,  $\Delta_r S_m$ ,  $\Delta_r G_m$  and  $q_r$  of the reaction for lithium ion cell measured by the electrochemical-calorimetric method (313.15 K).

Samples	Rate (C)	$q_{total}$ (mJ)	$\Delta_r H_m$ (kJ mol <sup>-1</sup> )	$\Delta_r S_m^a$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta_r G_m^a$ (kJ mol <sup>-1</sup> )	$q_r^a$ (kJ mol <sup>-1</sup> )
LiFePO <sub>4</sub> <sup>b</sup>	0.2	-365.35	-5.550	2.768	-6.42	-0.867
	0.5	-1333.47	-21.560	-	-	-
	1.0	-2398.92	-41.280	-	-	-
LiMn <sub>2</sub> O <sub>4</sub> <sup>c</sup>	0.2	-133.61	-4.352	1.761	-4.903	-0.551
	0.5	-449.22	-11.560	-	-	-
	1.0	-540.40	-17.404	-	-	-
LiNi <sub>0.5</sub> Co <sub>0.2</sub> Mn <sub>0.3</sub> O <sub>2</sub>	0.2	-145.964	-4.040	1.728	-4.581	0.541
	0.5	-373.706	-10.820	-	-	-
	1.0	-503.899	-13.794	-	-	-

<sup>a</sup> To measure the reversible heat more accurately, a very small current density (<0.1 mA cm<sup>-2</sup>) was utilized to charge and discharge the test cell

<sup>b,c</sup> Thermodynamic parameters of LiFePO<sub>4</sub> and LiMn<sub>2</sub>O<sub>4</sub> were from the reference [2] (L. B. Song, Z. L. Xiao, L. J. Li, Q. Q. Zhou, *J. Solid. State Electrochem.*, 19 (2015) 2167).

#### 4. CONCLUSIONS

In this paper, we studied the thermal-electrochemical behaviors of various lithium ion batteries with different cathode materials using electrochemical-calorimetric technique. Charge-discharge rate was one of the key factors that affect the cycling performance, discharge capacity and releasing heat. As the charge discharge rate increased, the discharge platform reduced, and the cycling performance worse, the discharge capacity decreased and the releasing heat increased. The greater enthalpy change value ( $\Delta_r H_m$ ) was, the worse the battery safety. The greater the entropy change ( $\Delta_r S_m$ ) was, the greater the confusion degree, the worse the reversibility and the safety performance. The  $\Delta_r H_m$  and

$\Delta_r S_m$  of  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  batteries were the minimum, so the reversibility was best and safety performance was highest, followed by  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiFePO}_4$  was the worst. The  $\Delta_r S_m$  values of  $\text{LiFePO}_4$  battery,  $\text{LiMn}_2\text{O}_4$  battery, and  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$  cell were 276.8, 1.761, 1.728  $\text{J mol}^{-1} \text{K}^{-1}$ . Electrochemical calorimetry can be an effective method for evaluating the performance of positive electrode materials providing reference for the electric and thermal performance of batteries.

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