Thermal study on single electrodes in lithium-ion battery

Qian Huang, Manming Yan, Zhiyu Jiang *

Department of Chemistry, and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials,
Fudan University, Shanghai 200433, China

Abstract

The thermodynamic parameters: ΔG, ΔS and ΔH of Li_xC_6/1 M $LiPF_6$/$Li_{1-x}CoO_2$ battery reaction were measured by potentiometric method. The ΔS and reversible Peltier heat q_r of cathode and anode reactions in lithium-ion battery were calculated from the ΔS of Li/1 M $LiPF_6$/$Li_{1-x}CoO_2$ and Li/1 M $LiPF_6$/Li_xC_6 cell reactions, and the ΔS of Li electrode reaction, respectively. For Li electrode reaction, the ΔS and q_r were detected by both potentiometric and electrochemical-calorimetric methods.

For a fully charged Li_xC_6/1 M $LiPF_6$/$Li_{1-x}CoO_2$ battery during reversible discharge process, the overall reaction $Li_{1-x}CoO_2 + Li_xC_6 \rightarrow LiCoO_2 + 6C$ presents exothermal heat effect with ΔS of -29.78 J K^{-1} mol^{-1} and q_r of 8.874 kJ mol^{-1}. Furthermore, the cathode reaction $xLi^+ + xe^- + Li_{1-x}CoO_2 \rightarrow LiCoO_2$ shows larger exothermic effect with ΔS of -121.8 J K^{-1} mol^{-1} and q_r of 36.30 kJ mol^{-1}, and the anode reaction $Li_xC_6 \rightarrow xLi^+ + xe^- + 6C$ shows smaller endothermic effect with ΔS of 92.08 J K^{-1} mol^{-1} and q_r of -27.46 kJ mol^{-1}. The heat produced at the positive electrode reaction is about three times more than that of overall battery reaction.
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Keywords: Lithium-ion battery; $Li_{1-x}CoO_2$ electrode; Li_xC_6 electrode; Battery thermal effect; Peltier heat

1. Introduction

Lithium-ion batteries, with high energy density, high voltage and long cycle life, have been extensively used in the portable electronic devices, such as laptop computers, cellular phones and camcorders since the first successfully commercialized by Sony in 1991. Although lithium-ion battery systems with large power and energy density have been investigated for the potential applications of hybrid electrical vehicles (HEVs) and satellites, the practical application is limited because of thermal safety problem. The key issue lies in if the system with large capacity is kept running at high environment temperature or high discharge rate, the exothermic effect will induce the heat accumulation inside the cell, leading to thermal runaway and even the cell burning.

Therefore, thermal characteristics of lithium-ion battery have been studied to understand the heat-generated mechanism inside the cell. The heat produced in the charge/discharge process of lithium-ion battery consists of irreversible and reversible two parts. The irreversible heat includes polarization heat and Joule heat. The reversible one (Peltier heat) is associated with the entropy change of the cell reaction [1]. The heat generated during the charge and discharge processes of commercial lithium-ion batteries has been directly measured by using electrochemical-calorimetric method, such as twin-type heat conduction calorimetry [2–5], accelerate-rate calorimetry (ARC) [6–9] and isothermal microcalorimetry (IMC) [10–12]. The entropy change of Li-ion intercalation reaction has been measured as a function of state of charge (SOC) by using potentiometric method [5–8,13]. Moreover, thermal stabilities of Li-ion cells and their components have been studied by using thermal analysis techniques, such as differential scanning calorimetry (DSC) [14–18] and thermogravimetric analysis (TGA) [15–17]. Various thermal models [19–22] for a single cell or cell stacks have also been developed to explain the experimental phenomena.

* Corresponding author. Tel.: +86 21 65642404; fax: +86 21 65641740.
  E-mail address: zyjiang@fudan.ac.cn (Z. Jiang).

Up to now, most thermal study of lithium-ion battery just focuses on the total heat effect for commercial lithium-ion battery, but the reversible heat produced at the positive or negative electrode, respectively, in a lithium-ion battery has not been reported, although it is very important to optimize the thermal design of Li-ion battery system with large capacity.

In this work, the integrated thermodynamic parameters for lithium-ion battery were studied. In particular, the reversible heat effects of single electrode reactions: positive and negative electrode reactions, respectively, inside the lithium-ion battery were investigated by both potentiometric and electrochemical-calorimetric methods.

2. Experimental

2.1. Thermodynamic study on lithium-ion battery by potentiometric measurement

A three-chamber cell was assembled in a glove box. The positive electrode contained 79 wt.% $LiCoO_2$, 11 wt.% carbon and 10 wt.% poly(vinyl difluoride) (PVdF) binder, coated on an Al foil substrate. The negative electrode contained 91 wt.% MCMB and 9 wt.% PVdF binder, coated on a Cu foil substrate. A lithium metal sheet was used as reference electrode and 1 M $LiPF_6$ in 1:1 (v/v) ethylene carbonate (EC)/dimethyl carbonate (DMC) (Merck) was used as electrolyte.

The $Li_xC_6/Li_{1-x}CoO_2$ cell was firstly charged to 4.20 V and cycled twice between 2.75 and 4.20 V with a constant current density of 0.1 mA cm^{-2} at room temperature 298 K. After charged to 4.20 V and kept at constant 4.20 V for 3 h (SOC = 1), the test cell was at the open circuit for about 24 h, relaxing to a relatively stable state. Then, the three-chamber cell was transferred to a non-aqueous oil-bath system, which was designed to control the temperature of the cell. The system temperature was programmed to increase from 298 to 318 K step-by-step and maintained at every measure point (T = 298, 303, 308, 313 and 318 K) for about two hours in order to reach a relatively stable state. Then, the open-circuit voltage E_{oc} at every test temperature was measured by UJ-25 potentiometer and its value could be considered as the equilibrium voltage E_{eq} [6]. Thus, the entropy coefficient dE_{eq}/dT for $Li_xC_6/1$ M $LiPF_6/Li_{1-x}CoO_2$ cell was obtained, so as for Li/1 M $LiPF_6/Li_{1-x}CoO_2$ and Li/1 M $LiPF_6/Li_xC_6$ cells. The thermodynamic parameters: Gibbs free energy change ΔG, entropy change ΔS, Peltier heat q_r (heat produced in the reversible reaction) and enthalpy change ΔH for the three cell reactions were, respectively, calculated by the equations as follows:

$$\Delta G = -nE_{eq}F \tag{1}$$

$$\Delta S = nF \left(\frac{dE_{eq}}{dT} \right) \tag{2}$$

$$q_r = -T \Delta S \tag{3}$$

$$\Delta H = \Delta G + T \Delta S \tag{4}$$

where $n = 1$ and F is the Faradic constant.

2.2. ΔS measurement for $Li \rightarrow Li^+ + e^-$ reaction

It should be mentioned that the ΔS of Li/1 M $LiPF_6/Li_{1-x}CoO_2$ and Li/1 M $LiPF_6/Li_xC_6$ cell reactions are not equal to the ΔS of single electrode reactions in lithium-ion battery. However, the Li/1 M $LiPF_6/Li_{1-x}CoO_2$ cell reaction $xLi + Li_{1-x}CoO_2 \rightarrow LiCoO_2$ consists of reaction $xLi^+ + xe^- + Li_{1-x}CoO_2 \rightarrow LiCoO_2$ and Li electrode reaction $Li \rightarrow Li^+ + e^-$. The Li/1 M $LiPF_6/Li_xC_6$ cell reaction $xLi + 6C \rightarrow Li_xC_6$ consists of reaction $xLi^+ + xe^- + 6C \rightarrow Li_xC_6$ and Li electrode reaction $Li \rightarrow Li^+ + e^-$. For lithium-ion battery, the single electrode reactions are:

Cathode reaction $\quad xLi^+ + xe^- + Li_{1-x}CoO_2 \rightarrow LiCoO_2$

(5)

Anode reaction $\quad Li_xC_6 \rightarrow xLi^+ + xe^- + 6C \tag{6}$
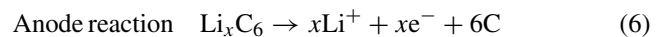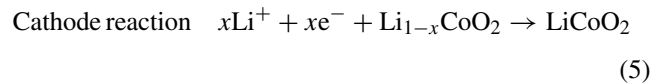
Therefore, the key to measuring the ΔS of single electrode reactions in lithium-ion battery comes down to the ΔS measurement for $Li \rightarrow Li^+ + e^-$ reaction.

Two kinds of methods, potentiometric and electrochemical-calorimetric measurements were proposed to measure the ΔS for $Li \rightarrow Li^+ + e^-$ reaction. Potentiometric method was by measuring the entropy coefficient (dE_{eq}/dT) for Li electrode reaction. Electrochemical-calorimetric method was direct to measure the heat produced by Li electrode during charge and discharge processes in a calorimeter.

2.2.1. Potentiometric measurement

The test cell consisted of two single-electrode tubes containing identical lithium sheet electrode for each other. The electrode tubes were separately placed in two oil-bath systems at different temperatures T_1 and T_2. A plastic tube full of 1 M $LiPF_6/EC$, DMC (1:1) electrolyte was used to connect two electrodes.

Electrode (T_1)/electrolyte (T_1)/electrolyte (T_2)/electrode (T_2)

Electrode: Li; electrolyte: 1 M $LiPF_6/EC$, DMC (1:1)

One system temperature (T_1) was fixed at 298 K. The other temperature (T_2) was programmed to increase from 298 to 323 K step-by-step and maintained at every test temperature (298, 303, 308, 313, 318 and 323 K) for about 2 h in order to reach a relatively stable state at every measure point. Then the potential difference ($\Delta E = E_2 - E_1$) at every temperature difference ($\Delta T = T_2 - T_1$) between two Li electrodes was measured by UJ-25 potentiometer and the entropy coefficient (dE_{eq}/dT) of Li electrode was obtained.

For Li electrode reaction $Li \rightarrow Li^+ + e^-$ in 1 M LiPF$_6$/EC, DMC (1:1) electrolyte, the entropy change $\Delta S_{Li^+/Li}$ and the corresponding Peltier heat $q_{Li^+/Li}$ could be calculated by equations (7) and (8):

$$\Delta S_{Li^+/Li} = F\left(\frac{dE_{eq}}{dT}\right) \qquad (7)$$

$$q_{Li^+/Li} = -T\,\Delta S_{Li^+/Li} \qquad (8)$$

2.2.2. Electrochemical-calorimetric measurement

The test cell was composed of two identical Li sheet electrodes with area of 1 cm^2. One Li electrode was fixed in a copper mold and put in a RD-1 heat conduction calorimeter. The use of copper mold was due to its good thermal conductivity. The other Li electrode tube was placed outside the calorimeter. A plastic tube full of 1 M LiPF$_6$/EC, DMC (1:1) electrolyte was used to connect two electrodes. During charge and discharge processes at low current density (0.1 mA cm^{-2}), the heat q_{ch} and q_{disch} generated by the Li electrode located inside the calorimeter were measured, respectively. Then, the ΔS for Li electrode could be calculated by comparison with the heat q_{ch} and q_{disch}. The calculation was based on the energy balances as follows [6]:

$$q_{ch} = q_{re,ch} + q_{irr,ch} \qquad (9)$$

$$q_{disch} = q_{re,disch} + q_{irr,disch} \qquad (10)$$

where the footnotes re and irr correspond to the reversible and irreversible processes, respectively. For charge and discharge processes, $q_{re,disch} = -q_{re,ch}$ and equals $-T\,\Delta S$. The irreversible heat equals $I\eta t + I^2 Rt$, where I, η, R and t are the current, the absolute value of electrode polarization, the Ohmic resistance of electrode and the time, respectively.

Irreversible heat is always an exothermic effect whatever in charge or discharge process. In general, the irreversible heat is much larger than the reversible heat, which leads to an exothermic heat effect apparently no matter in charge or discharge process. With the small polarization, the irreversible heat is in proportion to I^2 and the reversible heat is in proportion to current I. In order to measure the reversible heat more accurately, we used very small current density (0.1 mA cm^{-2}) to charge and discharge the test cell.

It is well known that at low current density the η values can be considered as the same for charge and discharge processes at same current density, so it could be assumed that $q_{irr,disch} = q_{irr,ch}$. Thus, $\Delta S_{Li^+/Li}$ can be calculated by

equation (11):

$$\Delta S = \frac{q_{ch} - q_{disch}}{2T} \qquad (11)$$

2.3. ΔS measurement for single electrode reactions in lithium-ion battery

Based on the ΔS for the reactions of Li/1 M LiPF$_6$/Li$_{1-x}$CoO$_2$ and Li/1 M LiPF$_6$/Li$_x$C$_6$ cells, and the ΔS for $Li \rightarrow Li^+ + e^-$ reaction, the ΔS for cathode and anode reactions: $xLi^+ + xe^- + Li_{1-x}CoO_2 \rightarrow LiCoO_2$ and $Li_xC_6 \rightarrow xLi^+ + xe^- + 6C$ in 1 M LiPF$_6$ EC:DMC = 1:1 solution could be calculated, respectively.

3. Results and discussion

3.1. Thermodynamic study on lithium-ion battery by potentiometric measurement

The equilibrium voltages for fully charged Li$_x$C$_6$/1 M LiPF$_6$/Li$_{1-x}$CoO$_2$, Li/1 M LiPF$_6$/Li$_{1-x}$CoO$_2$ and Li/1 M LiPF$_6$/Li$_x$C$_6$ cells were, respectively, measured by UJ-25 potentiometer at every test temperature (298, 303, 308, 313 and 318 K), as mentioned previously. The equilibrium voltages as a function of temperature for the three cells are shown in Fig. 1. The curves present linear relationships between equilibrium voltage and temperature. Thus, the thermodynamic parameters: ΔG, ΔS, q_r and ΔH values for the reactions of three above-mentioned cells were calculated by equations (1)–(4), respectively, as listed in Table 1.

The entropy coefficient for the reaction of Li$_x$C$_6$/1 M LiPF$_6$/Li$_{1-x}$CoO$_2$ cell is -0.3086 mV K^{-1} at $E_{eq} = 3.906$ V, which is in good agreement with the values in references [7,8] measured for Panasonic (18650H) cell. The entropy coefficient for Li/1 M LiPF$_6$/Li$_x$C$_6$ cell is 0.2158 mV K^{-1} at $E_{eq} = 0.1347$ V, just within the reported value range of 0.20–0.27 mV K^{-1} for Li/1 M LiPF$_6$/MCMB cell nearly at SOC = 1 [12]. Moreover, the ΔS calculated from the entropy coefficient is -29.78 J K^{-1} mol^{-1} for the reaction of Li$_x$C$_6$/1 M LiPF$_6$/Li$_{1-x}$CoO$_2$ cell at SOC = 1 (in Table 1) is close to the reported value -28 J K^{-1} mol^{-1} for Sony (US18650) cell [5].

The entropy values in Table 1 suggest that during the discharge process for a fully charged Li$_x$C$_6$/1 M LiPF$_6$/Li$_{1-x}$CoO$_2$ battery, the reversible process,

Table 1
E_{eq}, ΔG, ΔS, q_r and ΔH of the reactions for fully charged Li$_x$C$_6$/1 M LiPF$_6$/Li$_{1-x}$CoO$_2$, Li/1 M LiPF$_6$/Li$_{1-x}$CoO$_2$ and Li/1 M LiPF$_6$/Li$_x$C$_6$ cell measured by potentiometric method (298 K)

Cell system	Cell reaction	E_{eq} (V)	ΔG (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})	q_r (kJ mol^{-1})	ΔH (kJ mol^{-1})
Li$_x$C$_6$/Li$_{1-x}$CoO$_2$	Li$_x$C$_6$ + Li$_{1-x}$CoO$_2$ → LiCoO$_2$ + 6C	3.906	−376.8	−29.78	8.874	−385.7
Li/Li$_{1-x}$CoO$_2$	xLi + Li$_{1-x}$CoO$_2$ → LiCoO$_2$	4.040	−389.8	−8.857	2.639	−392.4
Li/Li$_x$C$_6$	xLi + 6C → Li$_x$C$_6$	0.1347	−12.99	20.82	−6.204	−6.786
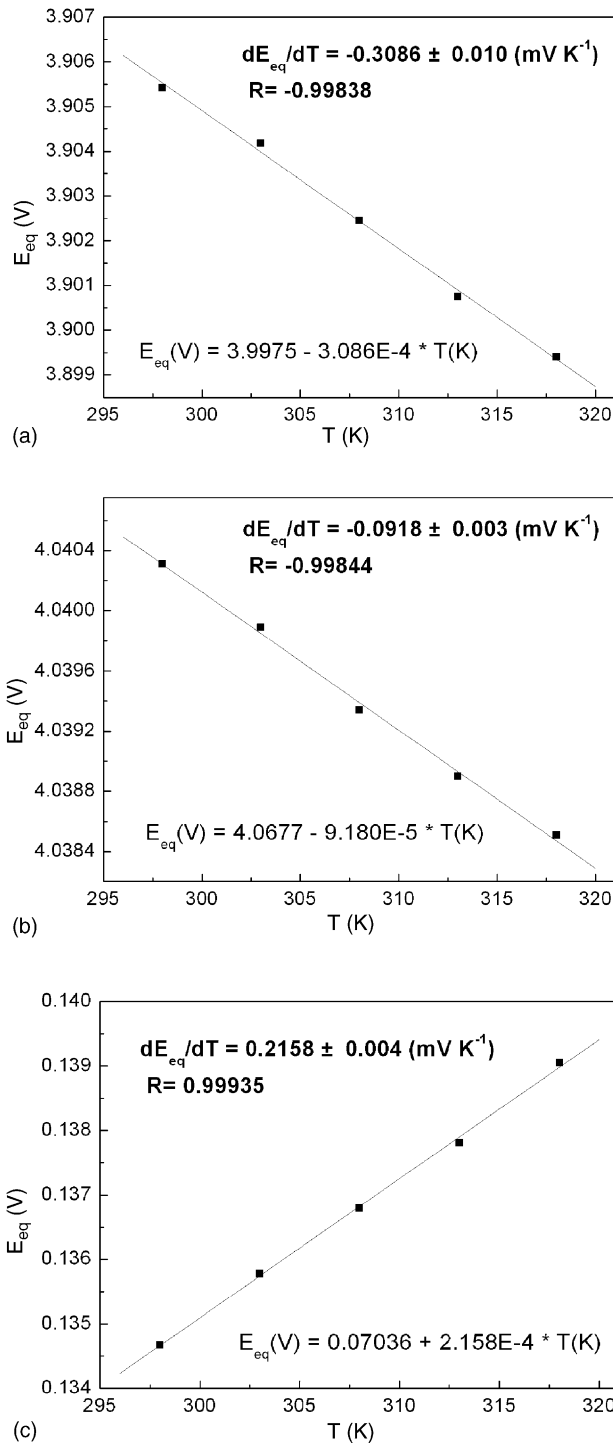
Fig. 1. Equilibrium voltage as a function of temperature for: (a) Li_xC_6/1 M $LiPF_6$/$Li_{1-x}CoO_2$, (b) Li/1 M $LiPF_6$/$Li_{1-x}CoO_2$ and (c) Li/1 M $LiPF_6$/Li_xC_6 cells.

$Li_{1-x}CoO_2 + Li_xC_6 \rightarrow LiCoO_2 + 6C$, is an exothermic reaction with ΔS of $-29.78 \, J \, K^{-1} \, mol^{-1}$. For Li/1 M $LiPF_6$/$Li_{1-x}CoO_2$ cell, the reversible reaction $xLi + Li_{1-x}CoO_2 \rightarrow LiCoO_2$, shows small exothermic heat effect, with ΔS of $-8.857 \, J \, K^{-1} \, mol^{-1}$. And for Li/1 M

$LiPF_6$/Li_xC_6 cell, the reversible reaction $xLi + 6C \rightarrow Li_xC_6$ shows relatively endothermic heat effect, with ΔS of $20.82 \, J \, K^{-1} \, mol^{-1}$.

As shown in Table 1, the values of ΔG and ΔH for the reaction of Li_xC_6/1 M $LiPF_6$/$Li_{1-x}CoO_2$ cell are -376.8 and $-385.7 \, kJ \, mol^{-1}$, respectively. ΔG is the energy value, which can be converted ideally into electric energy. So, during the reversible discharge process of a Li_xC_6/1 M $LiPF_6$/$Li_{1-x}CoO_2$ cell, the conversion efficiency of electric energy is $\Delta G/\Delta H = 97.7\%$. This is a high conversion efficiency of electric energy for batteries.

During the reversible discharge in the energy exchange from ΔH to ΔG, the residual energy $T\Delta S$ is compensated as the heat energy, just described as Peltier heat q_r in this paper. In Table 1, the Peltier heat produced during the reversible discharge process of a Li_xC_6/1 M $LiPF_6$/$Li_{1-x}CoO_2$ cell is $8.874 \, kJ \, mol^{-1}$. It can be calculated that this reversible heat effect is corresponding to the irreversible heat generated when the polarization value (η) is:

$$\eta = \frac{q_r}{F} = 0.092 \, V \tag{12}$$

in which the Joule heat is omitted.

It is known that the average heat capacity (C_p) of a commercial 18650 type Li_xC_6/$Li_{1-x}CoO_2$ battery is about $0.9 \, J \, g^{-1} \, K^{-1}$ [6]. Suppose the weight (W) of 18650 type Li_xC_6/$Li_{1-x}CoO_2$ battery is 40 g and the cell is kept discharging at 1 A for 5 min, the temperature rise (ΔT) caused by Peltier heat (q_r) can be calculated as:

$$\Delta T = \frac{q_r It}{FC_p W} = 0.77 \, {}^\circ C \tag{13}$$

where F is the Faradic constant.

In this case, the reversible heat effect during the discharge process of a Li_xC_6/$Li_{1-x}CoO_2$ battery cannot be neglected.

3.2. ΔS measurement for $Li \rightarrow Li^+ + e^-$ reaction

3.2.1. Potentiometric measurement

As mentioned above, the test cell consisted of two identical Li electrodes at different temperature T_1 and T_2, respectively. T_1 was a constant temperature (298 K) and T_2 varied. The potential difference ($\Delta E = E_2 - E_1$) at every temperature difference ($\Delta T = T_2 - T_1$) between two Li electrodes was measured by UJ-25 potentiometer. Fig. 2 shows a linear relationship between ΔE and ΔT. The slope of the line was the entropy coefficient (dE_{eq}/dT) of Li electrode in 1 M $LiPF_6$/EC, DMC (1:1) electrolyte. By using the thermodynamic equations (7) and (8), the ΔS and Peltier heat q_r of Li electrode reaction were, respectively, calculated, as listed in Table 2. The results suggest that the oxidation process for Li electrode, $Li \rightarrow Li^+ + e^-$, is an endothermic reaction, with ΔS of $112.9 \, J \, K^{-1} \, mol^{-1}$ and q_r of $-33.66 \, kJ \, mol^{-1}$.

Table 2
ΔS and Peltier heat q_r for the lithium electrode $Li \rightarrow Li^+ + e^-$ reaction in 1 M $LiPF_6$/EC, DMC (1:1) electrolyte (298 K)

Measurement	dE_{eq}/dT (mV K^{-1})	ΔS (J K^{-1} mol^{-1})	q_r (kJ mol^{-1})
Potentiometric method	1.17	112.9	−33.66
Electrochemical-calorimetric method	–	128.3	−38.26

Table 3
ΔS and q_r of single electrode reactions in Li_xC_6/1 M $LiPF_6$/$Li_{1-x}CoO_2$ battery (298 K)

System	Electrochemical reaction	ΔS (J K^{-1} mol^{-1})	q_r (kJ mol^{-1})
Overall cell	$Li_xC_6 + Li_{1-x}CoO_2 \rightarrow LiCoO_2 + 6C$	−29.78	8.874
Positive electrode	(+) $xLi^+ + xe^- + Li_{1-x}CoO_2 \rightarrow LiCoO_2$	−121.8	36.30
Negative electrode	(−) $Li_xC_6 \rightarrow xLi^+ + xe^- + 6C$	92.08	−27.44
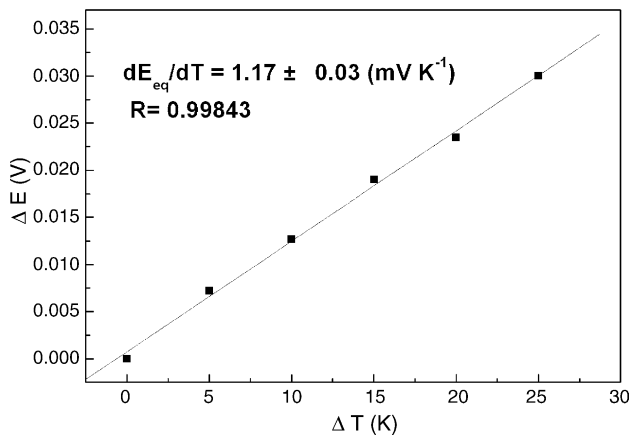
Fig. 2. ΔE as a function of ΔT between Li electrode (T_1) and Li electrode (T_2).

3.2.2. Electrochemical-calorimetric measurement

The thermal curve for one Li electrode inside the calorimeter during the cycling process at 0.1 mA cm^{-2} was recorded by measuring the thermal voltage (U) change, as shown in Fig. 3. Both charge and discharge curves presented exothermic behaviors. The heat q_{ch} or q_{disch} produced from this Li electrode was calculated by integrating the exothermic curve in charge period or discharge period, respectively, and using heat/thermal voltage conversion constant of the calorimeter. As mentioned above, by comparing the heat difference ($q_{disch} - q_{ch}$), the ΔS and q_r for the reaction $Li \rightarrow Li^+ + e^-$
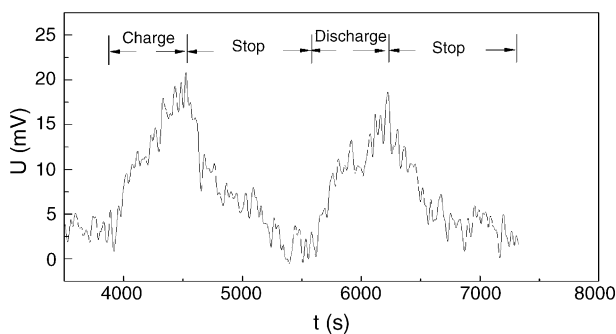
Fig. 3. Thermal curve for a Li electrode placed inside calorimeter during the cycling process at current density of 0.1 mA cm^{-2}.

could be calculated using equation (11) and also listed in Table 2. The results indicate that in 1 M $LiPF_6$/EC, DMC (1:1) electrolyte, the reaction $Li \rightarrow Li^+ + e^-$ is an endothermic reaction, with ΔS of 128.3 J K^{-1} mol^{-1} and q_r of −38.26 kJ mol^{-1}. The data from two methods agrees approximately. Considering that the η values for charge and discharge processes may not be quite equal, the electrochemical-calorimetric method may bring more error. So, the data from potentiometric method is adopted to calculate the ΔS and q_r of single electrode reactions in Li/1 M $LiPF_6$/$Li_{1-x}CoO_2$ battery.

3.3. ΔS measurement for single electrode reactions in lithium-ion battery

By combining $\Delta S_{Li^+/Li}$ and $q_{r,Li^+/Li}$ in Table 2 with the ΔS and q_r for Li/1 M $LiPF_6$/$Li_{1-x}CoO_2$ and Li/1 M $LiPF_6$/Li_xC_6 cell reactions in Table 1, the values of ΔS and q_r for single electrode reactions in Li/1 M $LiPF_6$/$Li_{1-x}CoO_2$ battery were calculated, as shown in Table 3. The results show that in the reversible discharge process for a fully charged Li_xC_6/1 M $LiPF_6$/$Li_{1-x}CoO_2$ battery, the positive electrode reaction, $xLi^+ + xe^- + Li_{1-x}CoO_2 \rightarrow LiCoO_2$ presents larger exothermic heat effect, with ΔS of −121.8 J K^{-1} mol^{-1} and q_r of 36.30 kJ mol^{-1}, meanwhile the negative electrode reaction, $Li_xC_6 \rightarrow xLi^+ + xe^- + 6C$ shows smaller endothermic heat effect, with ΔS of 92.08 J K^{-1} mol^{-1} and q_r of −27.46 kJ mol^{-1}. Therefore, it leads to the net exothermal heat effect in the overall lithium-ion battery.

It should be mentioned that the Peltier heat produced at the positive electrode is about three times more than that of overall battery (8.874 kJ mol^{-1}). Therefore, the large exothermic heat produced at the positive electrode is more important to be considered when optimizing thermal system design of a large capacity lithium-ion battery.

4. Conclusions

During the discharge process of a fully charged Li_xC_6/1 M $LiPF_6$/$Li_{1-x}CoO_2$ battery, the reversible cell discharge process, $Li_{1-x}CoO_2 + Li_xC_6 \rightarrow LiCoO_2 + 6C$, is an exother-

mic reaction with ΔS of $-29.78\,\mathrm{J\,K^{-1}\,mol^{-1}}$ and q_r of $8.874\,\mathrm{kJ\,mol^{-1}}$. Comparing with the irreversible heat, this reversible heat cannot be neglected. The positive electrode reaction, $x\mathrm{Li^+} + x\mathrm{e^-} + \mathrm{Li_{1-x}CoO_2} \rightarrow \mathrm{LiCoO_2}$, is an exothermic reaction, with ΔS of $-121.8\,\mathrm{J\,K^{-1}\,mol^{-1}}$ and negative electrode reaction, $\mathrm{Li_xC_6} \rightarrow x\mathrm{Li^+} + x\mathrm{e^-} + 6\mathrm{C}$, is an endothermic reaction, with ΔS of $92.08\,\mathrm{J\,K^{-1}\,mol^{-1}}$. The heat produced at the positive electrode is about three times more than that of overall battery, which should be taken into consideration when optimizing thermal system design for a high rate discharge lithium-ion battery.

Acknowledgement

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