Journal of Thermal Analysis and Calorimetry, Vol. 92 (2008) 2, 563–566

THERMAL PROPERTIES AND KINETICS STUDY OF CHARGED $LiCoO_2$ BY TG AND C80 METHODS

Q. S. Wang[1], *J. H. Sun*[1*], *C. H. Chen*[2] *and X. M. Zhou*[1]

[1]State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei 230026, P.R. China
[2]Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, P.R. China

The thermal stability of lithium-ion battery cathode could substantially affect the safety of lithium-ion battery. In order to disclose the decomposition kinetics of charged $LiCoO_2$ used in lithium ion batteries, thermogravimetric analyzer (TG) and C80 microcalorimeter were employed in this study. Four stages of mass losses were detected by TG and one main exothermic process was detected by C80 microcalorimeter for the charged $LiCoO_2$. The chemical reaction kinetics is supposed to fit by an Arrhenius law, and then the activation energy is calculated as E_a=148.87 and 88.87 kJ mol^{-1} based on TG and C80 data, respectively.

Keywords: *C80 microcalorimeter, kinetics, $LiCoO_2$, lithium ion battery, TG*

Introduction

Lithium-ion batteries are widely used in cell phones, laptop computers, and other portable electronic devices and have recently become available for power tools. However, their safety problems are getting more and more considerations, as the chemical reactions of the materials result in heat generation, which may lead to its thermal runaway, with venting of gas, fire, and finally battery rupture [1–7]. Layered $LiCoO_2$ is used as the cathode presently in most of the lithium ion cells due to its easy synthesis and excellent reversible lithium extraction/insertion properties. Therefore, an in-depth understanding of thermal behaviors and kinetics of charged $LiCoO_2$ is of significant importance for lithium ion batteries safety. The thermal behavior of lithium cobalt oxide has been investigated by differential scanning calorimetry (DSC) or accelerating rate calorimetry (ARC) [8–10]. However, the kinetics in few reported and more accurate information is required to better understand their decomposition kinetics. The C80 calorimeter allows to detect both exothermic and endothermic effect as well as to investigate the kinetic process of the related reactions, therefore, thermogravimetric analysis (TG) and the C80 calorimeter were used to study the thermal stability of charged $LiCoO_2$ used in lithium-ion battery in this paper.

Experimental

The electrolyte of 1.0 M $LiPF_6$/ethylene carbonate (EC) +diethyl carbonate (DEC) (1:1 mass%) were prepared in argon filled glove box. $LiCoO_2$ was produced by Tianjin Bamo Co. Ltd. The composition of the cathode was 84% of cathode, 8% of acetylene black and 8% of polyvinylidene fluoride (PVDF) binder. CR2032 coin cells were assembled in an argon-filled glove box with the $LiCoO_2$ as positive electrode, lithium as counter electrode, 1.0 M $LiPF_6$/EC+DEC as the electrolyte and Celgard 2400 polyethylene as the separator (20 μm thickness). The electrodes were dried over night in vacuum at 70°C and handled in an argon filled glove box (MBraun Labmaster 130, <1 ppm O_2 and H_2O). The electrodes were cut as a 14 mm diameter disk of about 400 μm thickness for get more mass of sample for C80 experiment. The $LiCoO_2$/Li cells were galvanostatically cycled three times on a multi-channel battery cycler (Neware BTS-6V10mA, Shenzhen) at room temperature, between 4.2 to 2.8 V at 0.2 mA cm^{-2} current density. After obtaining 4.2 V, a signature-charge test (equivalent to constant voltage charging) was used to stabilize the electrode at the desired voltage.

Then the charged cells (4.2 V) were disassembled in glove box. To remove the electrolyte from the electrode, the wet charged electrode powder was placed into a bottle. To that bottle a portion of dimethyl carbonate (DMC), a volatile organic solvent, was added and the bottle was then shaken by hand. The sample was then decanted and the DMC rinsing procedure was repeated. After the second decanting, the sample was dried to remove the DMC solvent. After drying, the electrode material was scraped, trying not to abrade the film, from the current collectors carefully for thermal test.

---

[*] Author for correspondence: sunjh@ustc.edu.cn

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

TG curves were measured using a STA490C thermal analyzer system at a heating/cooling rate of 10°C min^{-1} with 200 mL min^{-1} flow of N_2. About 10 mg of the powder sample were used as specimens and 99.99% pure α-Al_2O_3 powder was used as the standard material.

The prepared electrode was transferred into a high-pressure stainless steel vessel (8.5 mL in volume) of a microcalorimeter (Setaram C80) sealed in argon atmosphere. The samples were then removed from the glove box and analyzed in the C80. The mass of each sample (vessel+sample) was measured before and after the experiment to verify that the system was hermetically sealed. The mass was constant in all cases, indicating that there were no leaks during the experiments. The measurements were carried out using a heating rate set at 0.2°C min^{-1} in the temperature range 30–300°C in argon filled vessel. The thermal effects of each sample with temperature were thus recorded automatically, and the C80 calculations were based on dry film mass of the electrode material.

Results and discussion

Figure 1 is the TG plots of Li_xCoO_2 in N_2 flow at a heating rate of 10°C min^{-1} to 800°C, Li/$LiCoO_2$ cell was charged to 4.2 V, and x=0.52. There are four mass loss stages for Li_xCoO_2 in Fig. 1, which are signed by I (before 245°C), II (between 245 and 426°C), III (between 426 and 525°C) and IV (after 525°C), respectively. Based on our previous research [11, 12], the 1.0% mass loss before 245°C may be attributed to the loss of $LiPF_6$ or other contaminants. In stage II, the 3.76% loss may be attributed to the decomposition of PVDF and solid electrolyte interphase (SEI) that formed on electrodes surface [13]. In stage III, about 5.48% mass loss may be attributed to the acetylene carbon black decomposition. With the temperature increasing, in stage IV, Co_3O_4 decomposes and couples with the other reactions.

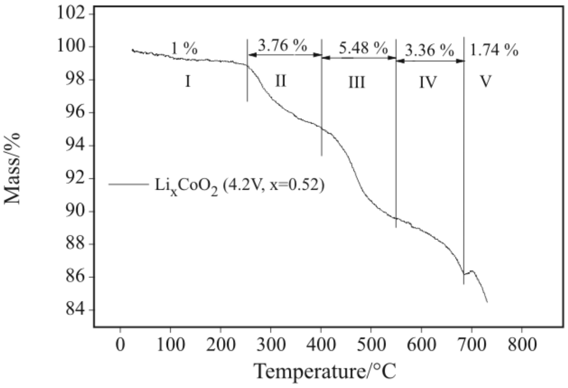

Fig. 1 TG plots of delithiated $LiCoO_2$ in N_2 flow at a heating rate of 10°C min^{-1}

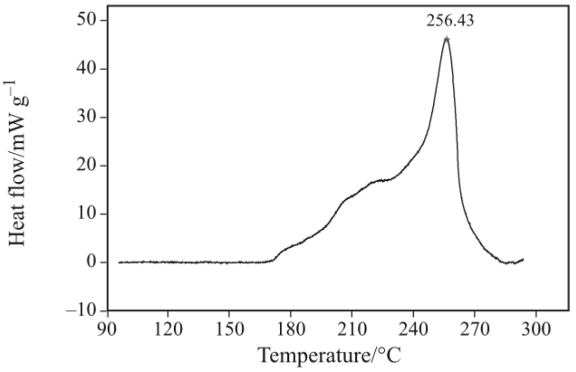

Fig. 2 C80 profiles of charged $LiCoO_2$ at a heating rate of 0.2°C min^{-1} in argon filled vessel

Figure 2 shows the thermal behaviors of Li_xCoO_2 at 4.2 V states of charge with a 0.2°C min^{-1} heating rate from 30 to 300°C in argon filled vessel. At the state of 4.2 V, Li_xCoO_2 starts to release heat at 171°C, and reaches to peak temperature at 256°C with a heat of reaction –489.0 J g^{-1}.

Kinetics

TG method

The kinetics of the reaction can be determined from the information given in a TG plot. For general homogeneous reactions of the type:

$$A\rightarrow B+C \tag{1}$$

the rate is determined from the following equation:

$$\text{rate}=k(F(\text{concentration of reactants and products}))_{T_{\text{constant}}} \tag{2}$$

Arrhenius equation:

$$k = A\mathrm{e}^{-E_a/RT} \tag{3}$$

describes the vaporization of the specific reaction rate with temperature. In the above equation k is the reaction rate and varies with temperature, E_a is the activation energy and A is the frequency factor. The terms E_a and A can be calculated [14]. In a solid-state reaction, then [15]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) \tag{4}$$

where α is the fraction decomposed at time t, $\mathrm{d}\alpha/\mathrm{d}t$ is the rate of the reaction, $k(T)$ is the reaction rate at temperature T, and $f(\alpha)$ is some function α. The term α has to be used in solid-state chemistry as concentration terms are meaningless in such circumstances. It is a term used by almost every worker studying the degradation of systems involving the solid-state [16]. Then, if:

$$T=T_0+\beta t \tag{5}$$

where T is temperature at time t, T_0 is the starting temperature, and β is the heating rate. The equations can be rearranged and combined to give the following:

$$k(T)=\frac{(\mathrm{d}\alpha/\mathrm{d}t)\beta}{f(\alpha)} \tag{6}$$

For a first-order reaction the equation for k is as follows:

$$k=\frac{\mathrm{d}\alpha/\mathrm{d}t}{1-\alpha} \tag{7}$$

By taking the natural logarithm of the Arrhenius equation:

$$\ln k = \ln A-\frac{E_\mathrm{a}}{RT} \tag{8}$$

and then combining the two equations the following is obtained:

$$\ln\left(\frac{\mathrm{d}\alpha/\mathrm{d}t}{1-\alpha}\right)=\ln A-\frac{E_\mathrm{a}}{RT} \tag{9}$$

From the plot obtained, the activation energy can be calculated from the slope of the line.

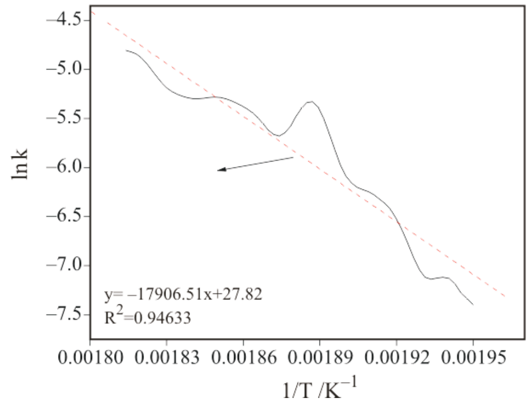

Fig. 3 ln$k$ *vs.* T^{-1} for the first stage of the decomposition of charged $LiCoO_2$

The activation energy of stage II in Fig. 1 was calculated from the plot of ln$k$ *vs.* T^{-1} in Fig. 3. The data in Fig. 3 gives the calculated results of E_a and A, they had the value of E_a=148.87 kJ mol^{-1}, A=1.22·10^{12} s^{-1}, respectively.

C80 method

In order to calculate the chemical kinetic parameters of reaction materials by using C80 data, a first-order reaction mechanism is assumed to be dependent on the Arrhenius law, so the rate expression for the consumption of reaction can be defined as Eq. (10).

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=A\exp\left(-\frac{E_\mathrm{a}}{RT}\right)(1-\alpha)^\mathrm{n} \tag{10}$$

where α is conversion rate.

Substituting α into Eq. (10), the next equation can be easily obtained.

$$-\frac{\mathrm{d}M}{M_0\mathrm{d}t}=A\exp\left(-\frac{E_a}{RT}\right)\left(\frac{M}{M_0}\right)^\mathrm{n} \tag{11}$$

Assuming it is the first-order reaction, that is n=1, at the initial stage the reactant consumption should be negligible. Therefore, M must be approximately equal to M_0. By multiplying Eq. (11) by the heat of reaction ΔH, the heat flow of the reaction is obtained as:

$$\frac{\mathrm{d}H/\mathrm{d}t}{\Delta HM_0}=A\exp\left(-\frac{E_\mathrm{a}}{RT}\right) \tag{12}$$

Taking natural logarithm of Eq. (12),

$$\ln\left(\frac{\mathrm{d}H/\mathrm{d}t}{\Delta HM_0}\right)=-\frac{E_\mathrm{a}}{R}\frac{1}{T}+\ln A \tag{13}$$

By plotting the curve of ln[(dH/dt)/ΔHM_0] *vs.* inverse temperature (T^{-1}), the activation energy (E_a) and frequency factor (A) can be easily calculated [17–19].

By this method, the plot of ln[(dH/dt)/ΔHM_0] *vs.* T^{-1} was drawn as Fig. 4, and the thermal decomposition activation energy and frequency factor of Li_xCoO_2 are calculated with the values of E_a=88.87 kJ mol^{-1}, A=1.87·10^6 s^{-1}, respectively.

The kinetics of charged $LiCoO_2$ can be calculated by the above two methods, however, there are little difference in the result. The value got from TG data is larger than that got from C80 data, which is supported by their thermal behavior plots respectively. The TG plot shows later onset temperature of mass loss, while the onset temperature of C80 plot is 171°C, which is much lower. From the fitted line in Figs 3 and 4, it also can be seen that the deviations got from the C80 result

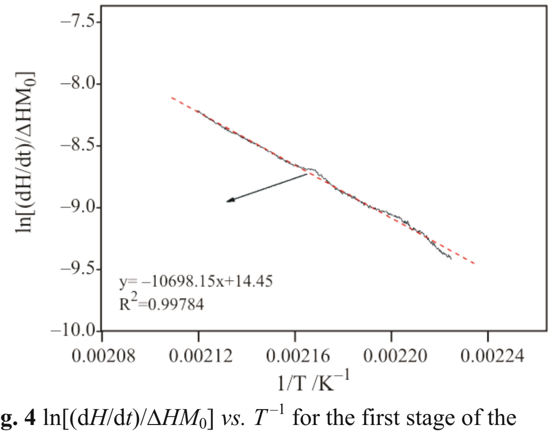

Fig. 4 ln[(dH/dt)/ΔHM_0] *vs.* T^{-1} for the first stage of the decomposition of charged $LiCoO_2$

is smaller than that of TG result, which indicated that C80 data result in more reliable result. It should be noted that the variation around the linear lines drawn in the plots of ln$k$ and ln[(dH/dt)/ΔHM_0] *vs.* T^{-1} are systematic and not random, which indicates that the reactions is apparent on the Arrhenius plots.

Conclusions

The stability of cathode and electrolyte plays a key role in lithium-ion battery safety, and $LiCoO_2$ is common used in lithium ion batteries as cathode. Therefore, the C80 calorimeter and TG technologies were employed in the thermal kinetics study of charged $LiCoO_2$. Both of the technologies show good performance in studying the thermal behaviors and kinetics of charged $LiCoO_2$. The reaction of charged $LiCoO_2$ is closely accordant on the Arrhenius plots, and then the activation energy is calculated as E_a=88.87 and 148.87 kJ mol^{-1} by C80 and TG data, respectively. Furthermore, it is speculated that the C80 data could result in more reliable kinetics.

Acknowledgements

This study was supported by National Science Foundation of China (grant No. 20603034) and Anhui College Science Research Program (KJ2007B262). Financial support from youth funds of USTC and Opening Fund os State Key Laboratory of Fire Science (grand No. HZ2006-KF10) are also appreciated.

References

1 M. Wakihara, Mater. Sci. Eng., R33 (2001) 109.
2 Q. S. Wang, J. H Sun, X. L. Yao and C. H. Chen, Thermochim. Acta, 437 (2005) 12.
3 P. G. Balakrishnan, R. Ramesh and T. P. Kumar, J. Power Sources, 155 (2006) 401.
4 S. Tobishima, K. Takei, Y. Sakurai and J. Yamaki, J. Power Sources, 90 (2000) 188.
5 Q. S. Wang, J. H. Sun, X. L. Yao and C. H. Chen, Electrochem. Solid-State Lett., 8 (2005) A467.
6 A. N. Jansen, A. J. Kahaian, K. D. Kepler, P. A. Nelson, K. Amine, D. W. Dees, D. R. Vissers and M. M. Thackeray, J. Power Sources, 81–82 (1999) 902.
7 Q. S. Wang, J. H. Sun, X. L. Yao and C. H. Chen, J. Loss Prevent. Process Ind., 19 (2006) 561.
8 Y. Baba, S. Okada and J. Yamaki, Solid State Ionics, 148 (2002) 311.
9 J. Jiang and J. R. Dahn, Electrochim. Acta, 49 (2004) 2661.
10 D. D. MacNeil and J. R. Dahn, J. Electrochem. Soc., 148 (2001) A1205.
11 Q. S. Wang, J. H. Sun, X. L. Yao and C. H. Chen, J. Electrochem. Soc., 153 (2006) A329.
12 Q. S. Wang, J. H. Sun D. L. Chen, and C. H. Chen, J. Alloys Compd. (in press).
13 A. Wursig, H. Buqa, M. Holzapfel, F. Krumeich and P. Novaka, Electrochem. Solid-State Lett., 8 (2005) A34.
14 K. W. Whitten, R. E. Davis and M. L. Peck, General Chemistry with Qualitative Analysis, 5th Ed., Saunders, New York 1996, pp. 623–629.
15 D. Dollimore, Thermochim. Acta, 340–341 (1999) 19.
16 L. Burnham, D. Dollimore and K. S. Alexander, Thermochim. Acta, 392–393 (2002) 127.
17 J. H. Sun, X. R. Li, K. Hasegawa and G. X. Liao, J. Therm. Anal. Cal., 76 (2004) 883.
18 Q. S. Wang, J. H. Sun, S. X. Lu, X. L. Yao and C. H. Chen, Solid State Ionics, 177 (2006) 137.
19 J. H. Sun, Y. F. Li and K. Hasegawa, J. Loss Prevent. Process Ind., 14 (2001) 331.

Received: January 4, 2007
Accepted: November 22, 2007

DOI: 10.1007/s10973-007-8289-z