

LiCoO₂ electrode/electrolyte interface of Li-ion batteries investigated by electrochemical impedance spectroscopy

ZHUANG QuanChao^{1,2}, XU JinMei¹, FAN XiaoYong¹, WEI GuoZhen¹, DONG QuanFeng¹, JIANG YanXia¹, HUANG Ling¹ & SUN Shigang^{1†}

¹ State Key Lab of Physical Chemistry of Solid Surfaces, Department of Chemistry, Xiamen University, Xiamen 361005, China;

² School of Materials Science and Engineering, China University of Mining & Technology, Xuzhou 221116, China

The storage behavior and the first delithiation of LiCoO₂ electrode in 1 mol/L LiPF₆-EC:DMC:DEC electrolyte were investigated by electrochemical impedance spectroscopy (EIS). It has found that, along with the increase of storage time, the thickness of SEI film increases, and some organic carbonate lithium compounds are formed due to spontaneous reactions occurring between the LiCoO₂ electrode and the electrolyte. When electrode potential is changed from 3.8 to 3.95 V, the reversible breakdown of the resistive SEI film occurs, which is attributed to the reversible dissolution of the SEI film component. With the increase of electrode potential, the thickness of SEI film increases rapidly above 4.2 V, due to overcharge reactions. The inductive loop observed in impedance spectra of the LiCoO₂ electrode in Li/LiCoO₂ cells is attributed to the formation of a Li_{1-x}CoO₂/LiCoO₂ concentration cell. Moreover, it has been demonstrated that the lithium-ion insertion-deinsertion in LiCoO₂ hosts can be well described by both Langmuir and Frumkin insertion isotherms, and the symmetry factor of charge transfer has been evaluated at 0.5.

Li-ion batteries, LiCoO₂, EIS, SEI film, inductance

The existence of chemical reactions at electrode-electrolyte interface in lithium batteries, which lead to decomposition of electrolyte components, was well-known since the 1960s. Later, it was suggested that the products of these reactions form a film on the surface of lithium metal and graphite electrodes. This surface film, often called a “passivating layer” or a “solid electrolyte interphase” (SEI)^[1–3], was found to play an important role in electrochemical processes occurring during lithium batteries cycling and has, therefore, attracted great scientific interests^[4–7].

The SEI formation is usually believed to take place only at the negative electrodes, such as metallic lithium or graphite compounds. In comparison with the research interests concerning the passivation of anodes, especially materials with carbonaceous origins, there have

been relatively few studies dedicated to the understanding of the interface formed between electrolytes and cathode surfaces. In recent years, more and more studies^[8,9] pointed out that the SEI film also exists on cathode surfaces, and it can affect significantly the electrochemical behavior of the cathode. On the one hand, the SEI film on the cathode surface can prevent the bulk electrolytes from further decompositions, and on the other hand, it also increases the resistance of the interface between the cathode and the electrolyte. Aurbach et al.^[10] reported that some degradation of the LiCoO₂ cathode may take place upon cycling. However, this

Received March 13, 2006; accepted August 17, 2006

doi: 10.1007/s11426-007-0088-7

†Corresponding author (email: sgsun@xmu.edu.cn)

Supported by the Special Funds for Major State Basic Research Project of China (Grant No. 2002CB211804)

degradation, while gradually decreasing the overall battery capacity, is not the major capacity fading mechanism of Li-ion batteries. The important factor that limits the cycle life of these batteries is an increase in the impedance of both the anode and the cathode, which relates to the formation and thickening of the SEI film. Liu et al.^[11] demonstrated that, by in situ synchrotron X-ray diffraction investigations, the Al₂O₃-coated LiCoO₂ experiences all the phase transitions that the bare LiCoO₂ does but with a better structural reversibility even if it is charged to 4.7 V versus Li⁺/Li. In brief, the electrochemical behavior of commonly used cathode materials for Li-ion batteries (such as LiCoO₂, LiNiO₂ and LiMn₂O₄) to some extent strongly depends on their surface chemistry in solutions, in a similar way as those found for electrochemical response of lithiated carbonaceous anodes in the same solutions.

In comparison with carbonaceous anode surfaces in Li-ion batteries, the surface of pristine cathode materials is often covered by a thick layer of Li₂CO₃, which is derived generally from material synthesis or due to continuous contact of lithiated oxides with atmosphere. When the cathode electrodes contact with non-aqueous organic electrolytes, spontaneous reactions may take place at surface of the cathode electrodes, the pristine Li₂CO₃ film and the active materials itself all can interact with electrolyte solution species. Such interaction may lead to a change in composition and in thickness of the SEI film that will be further changed upon cycling^[12-16]. Similar to early studies of the interface between lithium or carbonaceous electrodes and the electrolyte solutions, major works on the interface between cathodes and electrolyte solutions were focused on application of spectroscopic methods to characterize the composition of the SEI film and to figure out the formation mechanism. Electrochemical impedance spectroscopy, or EIS, is one of the most powerful means to analyze electrochemical processes occurring at electrode/electrolyte interfaces, and has been widely applied to investigate the SEI film formation process on carbonaceous material surfaces; it could also be applied to the analysis of the SEI film formation on cathode material surfaces^[12], especially the SEI film formation due to spontaneous reactions occurring at the surface of the cathode electrodes during its contact with non-aqueous organic electrolytes. To our knowledge, no such study has been reported so far. Moreover, the cathode electrodes used in the literature is often self-prepared for

different research purposes; it commonly differs from the cathode used in commercial Li-ion batteries in the composition and the manufacture process.

In the present study, LiCoO₂ cathode was prepared according to the composition and manufacture process employed in commercial Li-ion batteries, and the storage behavior as well as the process of first delithiation were investigated by EIS. The emphasis has been put upon the SEI film formation mechanisms, and the elucidation of the origin of inductance appeared in EIS spectra as well.

1 Experimental

All experiments were carried out in a three-electrode glass cell with Li foils as both auxiliary and reference electrodes. The LiCoO₂ electrode used in this study was prepared in Powerlong Battery Research Institute of Xiamen University by spreading a mixture of LiCoO₂ powder (B&M Ltd Co., Tianjin, China), carbon black (Shan-shan limited Co. Shanghai, China) and polyvinylidene fluoride (Kynar FLEX 2801, Elf-atochem, USA) binder dissolved in *N*-methyl pyrrolidone (Fluka Inc.) onto an aluminum foil current collector; the electrode composition was 92% active material, 3% carbon black and 5% polyvinylidene fluoride. The electrolyte was 1 mol/L LiPF₆-EC:DMC:DEC (volume ratio 1:1:1, Guotaihuarong Co., Zhangjiagang, China).

EIS measurements were carried out in an electrochemical work station (Par 2263-1, Princeton applied research, USA). The amplitude of ac perturbation signal was 5 mV and the frequency ranged from 10⁵ to 10⁻² Hz. The electrode was equilibrated for 2 h before EIS measurements.

2 Results and discussion

2.1 The common EIS features of LiCoO₂ electrode in storage and in the first delithiation

Variations of impedance spectra of LiCoO₂ electrode with the polarization potential in the first delithiation are shown in Figure 1. The Nyquist plots for the storage of LiCoO₂ electrode in electrolyte solutions at open circuit potential, 3.5 V, show an arc in the high-frequency (HF) range and a slightly inclined line in the low-frequency (LF) region. According to Aurbach et al.^[17,18], the HF arc is related to SEI film (R_{SEI} coupled with SEI film capacitance), and the slightly inclined line represents the

blocking character of the nondelithiated electrode at equilibrium potential due to the large charge transfer resistance coupled with double layer capacitance. Along with increasing the polarization potential, the slightly inclined line bends toward the real axis and forms a semicircle at 3.85 V; the spectrum at 3.9 V yields an HF arc related to SEI film as above, and a second arc in the medium-frequency (MF) region corresponding to charge transfer resistance coupled with double layer capacitance, followed by a straight line reflecting solid state Li-ion diffusion in the bulk of active mass. An important feature of the impedance spectra consists of the appearance of the inductive loop in the high to medium-frequency region at 3.95 V. The impedance spectra at 4.0 V include four fully separated parts, namely an HF arc, an inductive loop, an MF arc and a straight line in the low frequency region. The inductive loop and the straight line in the low frequency region disappear, and the MF arc converts to a slightly inclined line above 4.3

V, implying that there is no delithiation of Li ion from the active material in the above potential region.

2.2 Equivalent circuit proposed in EIS analysis

The equivalent circuit proposed to fit the EIS data that were obtained in initial storage in electrolyte and in subsequent first delithiation of the LiCoO₂ electrode is shown in Figure 2. In this equivalent circuit, R_s represents the ohmic resistance; R_{SEI} and R_{ct} are the resistances of the SEI film and the charge transfer reaction; the parallel resistance and the inductance are represented by R_L and L ; the capacitance of the SEI film, the capacitance of the double layer and the Warburg impedance are represented by the constant phase elements (CPE) Q_{SEI} , Q_{dl} and Q_D , respectively. The expression for the admittance response of the CPE (Q) is

$$Y = Y_0 \omega^n \cos\left(\frac{n\pi}{2}\right) + jY_0 \omega^n \sin\left(\frac{n\pi}{2}\right), \quad (1)$$

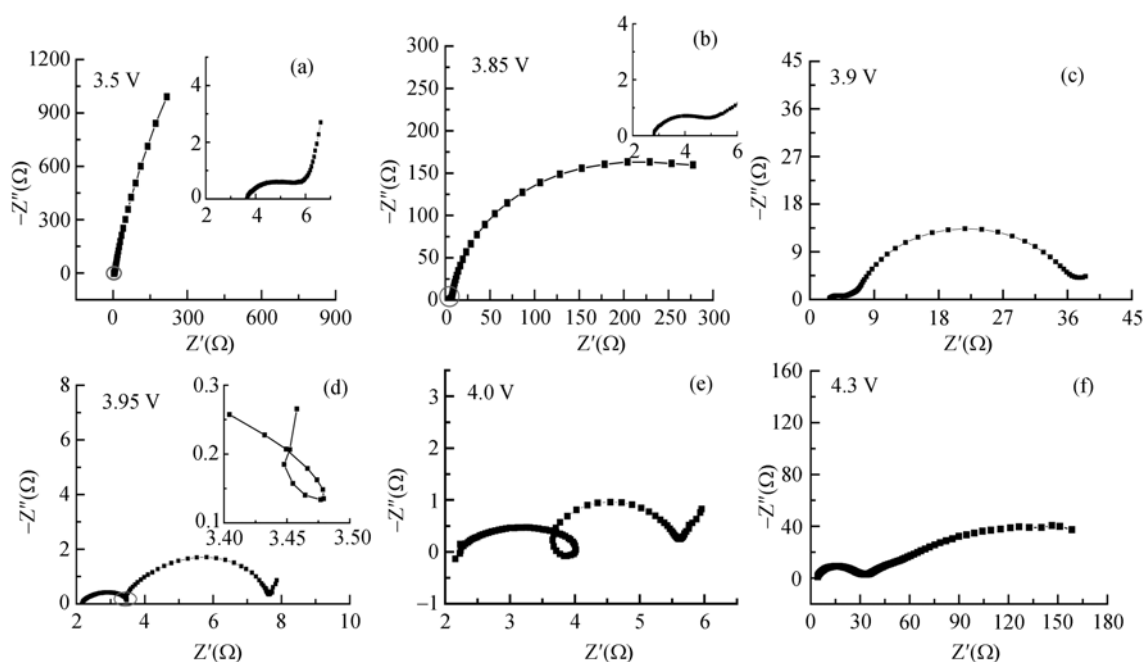


Figure 1 Variations of impedance spectra of LiCoO₂ electrode with the polarization potential in the first delithiation in frequency range 10^5 – 10^{-2} Hz.

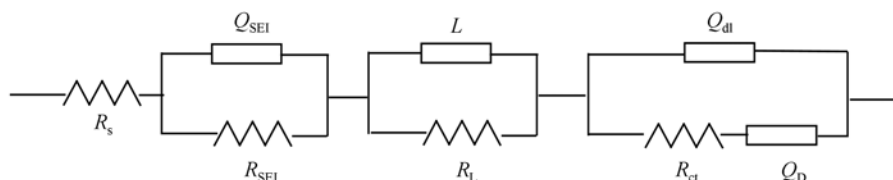


Figure 2 Equivalent circuit proposed for analysis of impedance spectra of LiCoO₂ electrode in the initial storage in electrolyte and in the first delithiation.

where ω is the angular frequency, and j the imaginary unit. A CPE represents a resistor when $n=0$, a capacitor with capacitance of C when $n=1$, an inductor when $n=-1$, and a Warburg resistance when $n=0.5$. In this study, Y_0 is considered to be a pseudo capacitance (pseudo- Y_0) when n lies between 0.5 and 1.

The simulated impedance spectra are compared with experimental EIS data at 4.05 V in Figure 3, and the values of parameters are listed in Table 1. It can be seen that the proposed model describes satisfactorily the experimental data. The relative standard deviation for all parameters fitted does not exceed 15%.

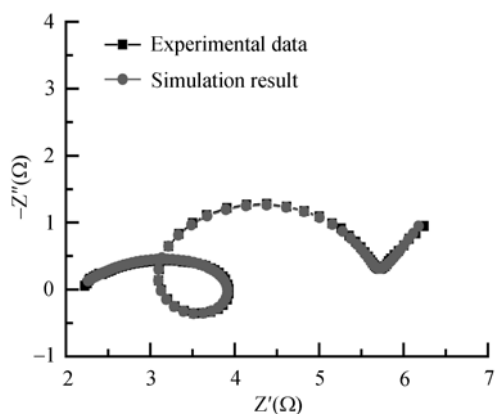


Figure 3 Comparison of EIS experimental data at 4.05 V with simulation results using equivalent circuit of Figure 2.

Table 1 Equivalent circuit parameters obtained from simulation of EIS experimental data at 4.05 V

Parameter	Value	Uncertainty (%)
R_s (Ω)	0.83486	4.6865
R_{SEI} (Ω)	2.253	2.5793
Q_{SEI-n}	0.50358	2.5050
Q_{SEI-Y_0} (F)	3.5728×10^{-3}	12.4030
R_{ct} (Ω)	2.572	1.8635
Q_{dl-n}	0.96045	1.3457
Q_{dl-Y_0} (F)	2.422×10^{-2}	2.6441
Q_D-n	0.66819	3.7617
Q_D-Y_0 (F)	5.929	7.5729
L (H)	5.7467×10^{-3}	4.1055
R_L (Ω)	2.561	4.6607
χ^2	8.5031×10^{-4}	

2.3 The mechanism of SEI film formation on LiCoO₂ electrode during storage and in the first delithiation

Figure 4 illustrates the variations of different EIS parameters obtained by fitting the experimental impedance spectra of the LiCoO₂ electrode with the increase of storage time in 1 mol/L LiPF₆-EC/DEC/DMC electro-

lyte. According to the SEI model, the resistance and capacitance values corresponding to the migration of Li ions through the SEI film are frequently described in the literature by using eqs. (2) and (3).

$$R = \rho l / S, \quad (2)$$

$$C = \epsilon S / l, \quad (3)$$

where l is the thickness of the SEI film, S the electrode surface area, ρ the resistivity, and ϵ the permittivity of the SEI film. It can be seen from Figure 4 that R_{SEI} increases with the increase of storage time, but its increasing rate declines with the increase of storage time. This result implies that, on the one hand, the thickness of the SEI film increases with the increase of storage time, and spontaneous reactions occurring between the LiCoO₂ electrode and the electrolyte were also prevented by the SEI film, on the other hand. Q_{SEI-Y_0} increases along with prolonging of the storage time, which indicates that the permittivity of the SEI film increases with time increasing, and that some high permittivity organic carbonate lithium compounds were formed on the LiCoO₂ electrode surface due to spontaneous reactions^[19]. Q_{SEI-n} decreases with the increase of the storage time, corresponding to the decrease of the homogeneity of the SEI film, probably also due to the formation of organic carbonate lithium compounds. Moreover, when the storage time is prolonged to 2 h, Q_{SEI-n} is less than 0.5, demonstrating that the LiCoO₂ electrode surfaces become extremely inhomogeneous and rough due to the formation of the SEI film.

Figure 5 displays variations of different EIS parameters with increase of electrode potential obtained from fitting the experimental impedance spectra of LiCoO₂ electrode in the first delithiation. It can be seen that, with the increase of electrode potential, R_{SEI} , Q_{SEI-n} and Q_{SEI-Y_0} keep invariable below 3.8 V, indicating that the SEI film remains persistent and stable to a certain extent after a long time of storage. When electrode potential is increased from 3.8 to 3.9 V, R_{SEI} and Q_{SEI-Y_0} decrease slowly, while Q_{SEI-n} increases slowly; on further increase of potential to 3.95 V, R_{SEI} and Q_{SEI-Y_0} decrease rapidly, but Q_{SEI-n} increases rapidly. The above phenomenon is commonly attributed to the reversible breakdown of the resistive SEI film^[8], because of limited studies carried out on cathode surfaces; there is no microscopic picture available for this breakdown mechanism. In comparison of Figure 4 with Figure 5, it can be found that the variations of R_{SEI} , Q_{SEI-n} and Q_{SEI-Y_0}

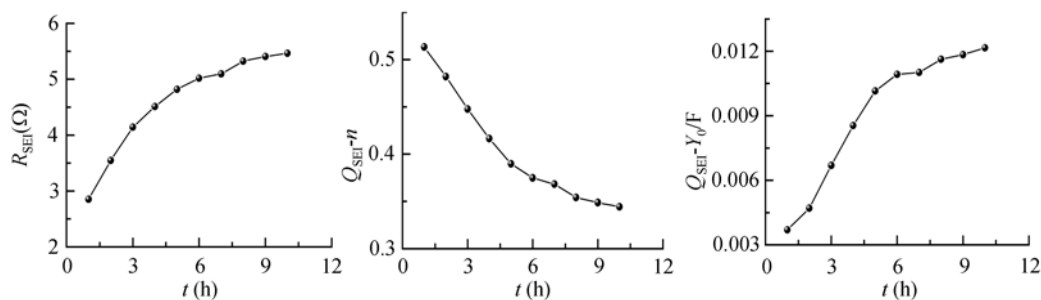


Figure 4 Variations of EIS parameters obtained from fitting the experimental impedance spectra of LiCoO₂ electrode with the increase of storage time at open circuit potential (OCP, 3.5 V).

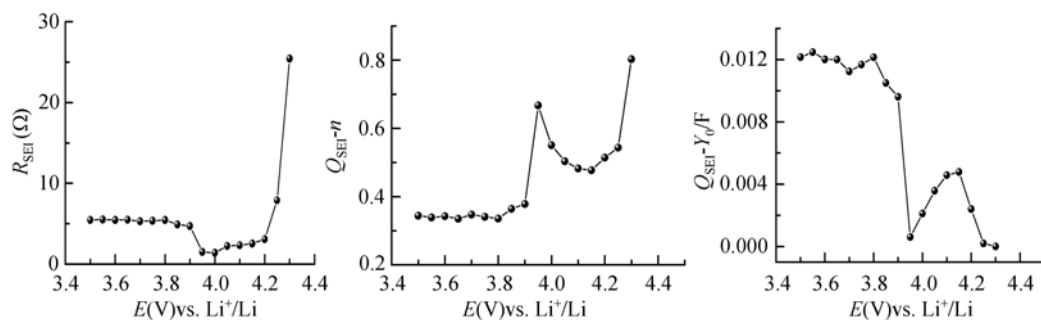


Figure 5 Variations of EIS parameters with the increase of the electrode potential obtained from fitting the experimental impedance spectra of LiCoO₂ electrode in the first delithiation.

in the first delithiation are contrary to those obtained in the storage, thus it can be concluded that the reversible breakdown of the resistive SEI film is probably due to the reversible dissolution of the SEI film components. With the potential changing from 4.0 to 4.2 V, R_{SEI} and Q_{SEI-Y_0} increase slowly, while Q_{SEI-n} decreases slowly, which are attributed to the reversible phase transition. When electrode potential is above 4.2 V, R_{SEI} and Q_{SEI-n} increase rapidly, but Q_{SEI-Y_0} decreases rapidly, demonstrating that the thickness of the SEI film increases rapidly. This should be obviously attributed to the oxidation of organic solvent because of overcharge. Therefore, the potential of LiCoO₂ electrode in charge-discharge cycles should be restrictedly limited below 4.2 V.

2.4 The mechanism of inductance formation of LiCoO₂ electrode in the first delithiation

It can be seen from Figure 1 that, the inductive loop first appears at 3.95 V, corresponding to the potential region where lithium ion begins to deintercalate from the LiCoO₂ electrode; when the electrode potential is above 4.3 V where lithium ion has fully deintercalated from the LiCoO₂ electrode, the inductive loop disappears. An inductance is defined as the properties of an electric cir-

cuit that causes an electromotive force to be generated in it as a result of a change in the current flowing through the circuit. Thus, a plausible explanation for the inductive loop is the formation of an electromotive force superimposed on the lithium ion deintercalation. Most likely it results from that, when lithium ions are deintercalated from the LiCoO₂ electrode, isolation of Li-rich and Li-poor (deficient) regions in the electrode may be created by the SEI film due to disequilibrium with respect to electronic continuity, thus a concentration cell is established between LiCoO₂ and delithiated LiCoO₂ (Li_{1-x}CoO₂, 0 < x < 0.5) separated by the SEI film. Because the SEI film is imperfect in the first delithiation of LiCoO₂, a current flows within the concentration cell, which generates a field that opposes the field due to the deintercalation reaction. The discharge of a concentration cell involves current flow opposed to charging the LiCoO₂ electrode, such a situation meets well with the requirements for the formation of an inductive loop. To understand an inductive loop in the cell, a pictorial model representation of the SEI film growth and the concentration cell is presented in Figure 6. With lithium ion deintercalation from the LiCoO₂ electrode in charge-

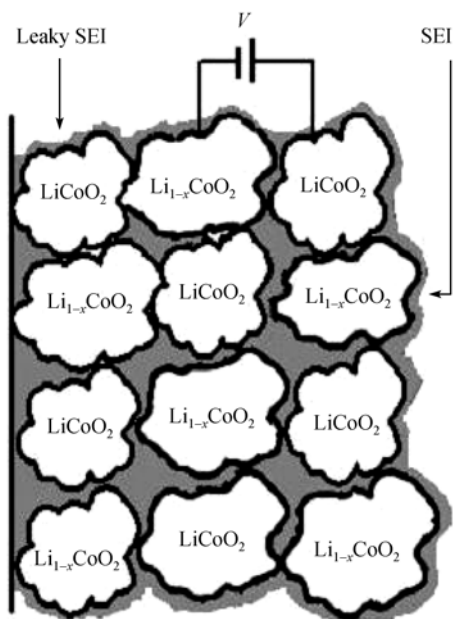


Figure 6 Pictorial representation model for the SEI film growth and the concentration cell.

discharge processes, the $\text{Li}_{1-x}\text{CoO}_2/\text{LiCoO}_2$ concentration cell continues to leak current until the electrode fully deintercalated (corresponding to LiCoO_2 fully converted to $\text{Li}_{0.5}\text{CoO}_2$), i.e., the lithium ion concentration differences in the electrode are removed. Thus, the SEI film on the LiCoO_2 electrode surface may be termed a “leak SEI film”. It can be seen from the above analysis that the experimental results obtained in this study can be satisfactorily interpreted by the model of $\text{Li}_{1-x}\text{CoO}_2/\text{LiCoO}_2$ concentration cell in the LiCoO_2 electrode. Moreover, it is worthwhile noting that Ganaraj et al. also attributes inductance to LiC_6/C_6 concentration cell in a Li/C cell^[20]. According to the above model of concentration cell, it can be predicted that, when half LiCoO_2 is converted into $\text{Li}_{0.5}\text{CoO}_2$, which corresponds to the maximum concentration polarization of lithium ions, the maximum inductance will be reached resulting from the $\text{Li}_{1-x}\text{CoO}_2/\text{LiCoO}_2$ concentration cell. It can be seen from Figure 7 that, with the increase of electrode potential, the maximum R_L and L were obtained at 4.05 and 4.15 V, respectively; this further demonstrates that the inductance in the Li/LiCoO_2 cell results from the $\text{Li}_{1-x}\text{CoO}_2/\text{LiCoO}_2$ concentration cell. In addition, we have prepared LiCoO_2 electrode by means of ball grinding. Since the equilibrium can be easily reached in the electrode, the inductance disappears in the EIS spectra. Furthermore, we have observed also the disappearance of the $\text{LiCoO}_2/\text{Li}_{1-x}\text{CoO}_2$ concentration cell along with

prolonging time after charging the LiCoO_2 electrode. These additional experimental evidences confirmed also that the $\text{LiCoO}_2/\text{Li}_{1-x}\text{CoO}_2$ concentration cell is the origin of producing the inductance.

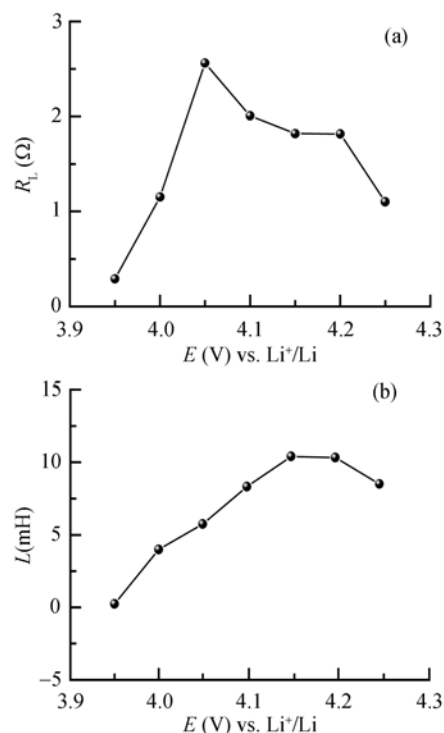


Figure 7 Variations of R_L and L with the increase of the electrode potential obtained from fitting the experimental impedance spectra of LiCoO_2 electrode in the first delithiation.

2.5 Variations of charge transfer resistance with electrode potential

The general expression for the charge transfer resistance is given by eq. (4).

$$R_{ct} = \frac{1}{\partial I_f / \partial E}, \quad (4)$$

where $\partial I_f / \partial E$ is the partial derivative of Faradaic current with respect to electrode potential and evaluated at steady state. It is well known that^[21], for insertion processes studied under blocking (restricted, finite space) diffusion conditions, steady state means the equilibrium state. Therefore, the charge transfer resistance can be written as

$$R_{ct} = \frac{1}{fFA\nu_0}, \quad (5)$$

where $f = F/RT$ (F and R , Faraday and gas constant, respectively, T , absolute temperature), A denotes the total electroactive surface area and ν_0 the exchange rate for the insertion reaction at equilibrium. $A\nu_0$ can be cal-

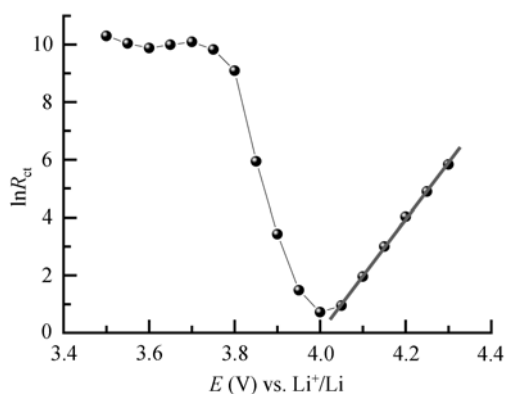


Figure 8 Variations of the logarithm of R_{ct} with the increase of the electrode potential.

culated from eq. (5) and the logarithm of the charge transfer resistance of the LiCoO_2 electrode plotted versus electrode potential as shown in Figure 8. A straight line is observed at high potential region, which indicates that the experimental values of v_0 shows an exponential dependence on electrode potential. According to

$$v_0 = k \exp(-\alpha f E), \quad (6)$$

a value of 0.5 for α is calculated from the straight line slope in Figure 8, which is consistent with the value of symmetry factor of charge transfer in electrochemical kinetics. Eq. (6) can be compared to the theoretical expression for the exchange rate of insertion processes, which depends on the insertion isotherm. The Frumkin isotherm was used for lithium-ion deintercalated from LiCoO_2 hosts assuming non-ideal behavior with interactions between the intercalated species^[17,22]. Under the above assumption, the exchange rate is given by the following:

$$v_0 = K_r M^+ c_T (1-x) \exp(-\alpha_r g x) = K_o c_T x \exp(\alpha_o g x), \quad (7)$$

with K_r and K_o as rate constants for the charge transfer of reduction and oxidation, respectively, i.e.,

$$K_o = k_o \exp(\alpha_o f E), \quad K_r = k_r \exp(-\alpha_r f E), \quad \alpha_o + \alpha_r = 1. \quad (8)$$

M^+ is the bulk concentration of lithium-ion in solutions, c_T the maximum (saturation) concentration of the inserted species in the LiCoO_2 host, α_o and α_r symmetry factors for the oxidation and reduction reaction, and g Frumkin interaction parameter. $g > 0$ corresponds to repulsive interactions and $g < 0$ to attractive interactions in the host material.

Setting $g=0$ in eq. (7), we obtain the Langmuir insertion isotherm in the absence of interactions between the intercalated species and the host material, on the one

hand, and between the intercalated species themselves, on the other.

Clearly, eq. (6) is the limiting form of eq. (7), which is obtained for very low insertion level ($x \rightarrow 0$, $E \rightarrow \infty$) with $k = k_r M^+ c_T$ and $\alpha = \alpha_r$. Therefore, both Langmuir and Frumkin insertion isotherms can describe the experimental results correctly, at least for very low insertion levels.

Setting $g=0$, $M^+=1$, $c_T=1$ and $\alpha_o = \alpha_r = 0.5$ in eq. (7), the exchange rate is given by the following:

$$v_0 = k_s x^{0.5} (1-x)^{0.5},$$

$$k_s = k_r \exp(-\alpha_r f E_0) = k_o \exp(-\alpha_o f E_0), \quad (9)$$

$$E_0 = \frac{1}{f} \ln \frac{k_o}{k_r}.$$

In this equation, k_s is the standard exchange rate constant, and x the intercalation level (i.e., the mole fraction of the species). When eq. (5) is introduced to eq. (9), the charge transfer resistance is given by the following:

$$R_{ct} = \frac{1}{f A k_s x^{0.5} (1-x)^{0.5}}. \quad (10)$$

Eq. (10) predicts clearly a rapid increase in R_{ct} with the decrease of x as $x < 0.5$, a rapid decrease in R_{ct} with the increase of x as $x > 0.5$, and the minimum R_{ct} can be attained when $x=0.5$. The Eq.(10) can be used to interpret properly the experimental data obtained above 3.7 V in this study, while the variation of $\ln R_{ct}$ with the increase of electrode potential can not be interpreted appropriately below 3.7 V, probably due to the strong interactions between the intercalated species and the host material, on the one hand, and between the intercalated species themselves, on the other hand, in the fully lithiated state of LiCoO_2 .

3 Conclusions

The storage behavior and first delithiation of LiCoO_2 electrode in 1 mol/L $\text{LiPF}_6\text{-EC:DMC:DEC}$ electrolyte were investigated by EIS. The results demonstrated that, with the increase of storage time, the thickness of SEI film increases, and some organic carbonate lithium compounds are formed on the LiCoO_2 electrode surfaces due to spontaneous reactions occurring between the LiCoO_2 electrode and electrolyte. When electrode potential is augmented from 3.8 to 3.95 V, the phenomenon of reversible breakdown of the resistive SEI film

occurs, which is attributed to the reversible dissolution of the SEI film components. With the increase of electrode potential, the thickness of SEI film increases rapidly above 4.2 V, due to overcharge reactions. Based on experimental data, it has suggested that the inductance appearing in EIS spectra may be resulted from the $\text{Li}_{1-x}\text{CoO}_2/\text{LiCoO}_2$ concentration cell in the Li/LiCoO_2

cell, which has been confirmed by both theoretical analysis and experimental results. The study has revealed also that the lithium-ion insertion-deinsertion in LiCoO_2 hosts can be well described by using both Langmuir and Frumkin insertion isotherms, according to which and from experimental data the symmetry factor of charge transfer is evaluated at 0.5.

- 1 Thevemin J G, Muller R H. Impedance of lithium electrode in a propylene carbonate electrolyte. *J Electrochem Soc*, 1987, 134(2): 273—280
- 2 Peled E, Goldnitsky D, Ardel G. Advanced model for solid electrolyte interphase of lithium electrode in liquid and polymer electrolytes. *J Electrochem Soc*, 1997, 144(8): L208—L210
- 3 Peled E. The electrochemical behavior of alkali and alkaline earth metals in nonaqueous battery systems—the solid electrolyte interphase model. *J Electrochem Soc*, 1979, 126(12): 2047—2051
- 4 Aurbach D, Weissman I, Schechter A. X-ray photoelectron spectroscopy studies of lithium surfaces prepared in several important electrolyte solutions. A comparison with previous studies with previous studies by fourier transform infrared spectroscopy. *Langmuir*, 1996, 12(16): 3991—4007
- 5 Schechter A, Aurbach D. X-ray photoelectron spectroscopy study of surface films formed on Li electrodes freshly prepared in alkyl carbonate solutions. *Langmuir*, 1999, 15(9): 3334—3342
- 6 Jeong S K, Inaba M, Iriyama Y, Abe T, Ogumi Z. Surface film formation on a graphite negative electrode in lithium-ion batteries: AFM study on the effects of co-solvents in ethylene carbonate-based solutions. *Electrochim Acta*, 2002, 47(12): 1975—1982
- 7 Morigaki K I. In situ analysis of the interfacial reactions between MCMB electrode and organic electrolyte solutions. *J Power Sources*, 2002, 103(2): 253—264
- 8 Xu K. Nonaqueous liquid electrolytes for lithium-based rechargeable batteries. *Chem Rev*, 2004, 104(10): 4303—4418
- 9 Würsig A, Buqa H, Holzzapfel M, Krumeich F, Novák P. Film formation at positive electrodes in lithium-ion batteries. *Electrochem Solid-State Lett*, 2005, 8(1): A34—A37
- 10 Aurbach D, Markovsky B, Rodkin A, Cojocar M, Elena Levi E, Kim H J. An analysis of rechargeable lithium-ion batteries after prolonged cycling. *Electrochim Acta*, 2002, 47(12): 1899—1911
- 11 Liu L, Chen L, Huang X, Yang X, Yoon W S, Lee H S, McBreen J. Electrochemical and *in situ* synchrotron XRD studies on Al_2O_3 -coated LiCoO_2 cathode material. *J Electrochem Soc*, 2004, 151(9): A1344—A1351
- 12 Aurbach D, Gamolsky K, Markovsky B, Salitra S, Gofer Y, Heider U, Oesten R, Schmidt M. The study of surface phenomena related to electrochemical lithium intercalation into Li_xMO_y host materials ($M=\text{Ni}, \text{Mn}$). *J Electrochem Soc*, 2000, 147(4): 1322—1331
- 13 Eriksson T, Andersson A M, Bishop A G, Gejke C, Gustafsson T, Thomas J O. Surface analysis of LiMn_2O_4 electrodes in carbonate-based electrolytes. *J Electrochem Soc*, 2002, 149(1): A69—A78
- 14 Matsuo Y, Kostecki R, McLarnon F. Surface layer formation on thin-film LiMn_2O_4 electrodes at elevated temperatures. *J Electrochem Soc*, 2001, 148(7): A687—A692
- 15 Ostrovskii D, Ronci F, Acrosati B, Jacobsson P. Reactivity of lithium battery electrode materials toward non-aqueous electrolytes: spontaneous reactions at the electrode-electrolyte interface investigated by FTIR. *J Power Sources*, 2001, 103(1): 10—17
- 16 Ostrovskii D, Ronci F, Scrosati B, Jacobsson P. A FTIR and Raman study of spontaneous reaction occurring at the $\text{LiNi}_x\text{Co}_{(1-x)}\text{O}_2$ electrode/non-aqueous electrolyte interface. *J Power Sources*, 2001, 94 (2): 183—188
- 17 Levi M D, Salitra G, Markovsky B, Teller H, Aurbach D, Heider U, Heider L. Solid-state electrochemical kinetics of Li-ion intercalation into $\text{Li}_{1-x}\text{CoO}_2$: simultaneous application of electroanalytical techniques SSCV, PITT, and EIS. *J Electrochem Soc*, 1999, 146(4): 1279—1289
- 18 Levi M D, Gamolsky K, Aurbach D, Levi M D, Gamolsky K, Aurbach D, Heider U, Oesten R. On electrochemical impedance of $\text{Li}_x\text{Co}_{0.2-x}\text{Ni}_{0.8}\text{O}_2$ and Li_xNiO_2 intercalation electrodes. *Electrochim Acta*, 2000, 45(11): 1781—1789
- 19 Wang Z, Huang X, Chen L. Characterization of spontaneous reactions of LiCoO_2 with electrolyte solvent for lithium-ion batteries. *J Electrochem Soc*, 2004, 151(10): A1641—A1652
- 20 Gnanaraj J S, Thompson R W, Iaconatti S N, DiCarlo J F, Abraham K M. Formation and growth of surface films on graphitic anode materials for Li-ion batteries. *Electrochem Solid-State Lett*, 2005, 8(2): A128—132
- 21 Montella C. Review and theoretical analysis of ac-av methods for the investigation of hydrogen insertion I. Diffusion formalism. *J Electrochem Chem*, 1999, 462(2): 73—87
- 22 Holzzapfel M, Martinet A, Allion F, Holzzapfel M, Martinet A, Alloin F, Le Gorrec B, Yazami R, Montella C. First lithiation and charge/discharge cycles of graphite materials, investigated by electrochemical impedance spectroscopy. *J Electroanal Chem*, 2003, 546: 41—50