

## Impedance Studies of Spinel $\text{LiMn}_2\text{O}_4$ Electrode/electrolyte Interfaces

ZHUANG Quan-chao<sup>1,2</sup>, FAN Xiao-yong<sup>2</sup>, XU Jin-mei<sup>2</sup>, WEI Guo-zhen<sup>2</sup>,  
DONG Quan-feng<sup>2</sup> and SUN Shi-gang<sup>2\*</sup>

1. School of Materials Science and Engineering, China University of Mining & Technology,  
Xuzhou 221116, P. R. China;

2. State Key Laboratory of Physical Chemistry of Solid Surfaces, Department of Chemistry,  
Xiamen University, Xiamen 361005, P. R. China

**Abstract** The formation process of solid electrolyte interphase(SEI) film on spinel  $\text{LiMn}_2\text{O}_4$  electrode surface was studied by electrochemical impedance spectroscopy(EIS) during the initial storage in 1 mol/L  $\text{LiPF}_6\text{-EC:DMC:DEC}$  electrolyte and in the subsequent first charge-discharge cycle. It has been demonstrated that the SEI film thickness increased with the increase of storage time, and spontaneous reactions occurring between spinel  $\text{LiMn}_2\text{O}_4$  electrode and electrolyte can be prevented by the SEI film. In the first charge-discharge cycle succeeding the storage, the electrolyte oxidation coupled with Li-ion insertion is evidenced as the main origin to increase the resistance of SEI film. The results also confirm that the variations of the charge transfer resistance( $R_{ct}$ ) with the electrode potential( $E$ ) can be well described using a classical equation.

**Keywords** Li-ion batteries; SEI film; Electrochemical impedance spectroscopy; Spinel  $\text{LiMn}_2\text{O}_4$

### 1 Introduction

Li-ion batteries, employing lithium-metal-oxygen materials( $\text{LiMO}_2$ , where,  $M=\text{Co}$ ,  $\text{Ni}$ ,  $\text{Mn}$ , and other metals) as positive electrodes and carbon materials as negative electrodes, are attractive owing to their high energy density and high power density, and are widely used for supplying electrical energy to portable electronic devices and (hybrid) electric vehicles<sup>[1–3]</sup>. Since the initial commercialization of Li-ion batteries in 1990<sup>[1]</sup>, intense efforts in research and development have been sustained to improve the performances of the batteries.

The unsatisfactory problems such as the capacity fade and self-discharge during cycling and storage, especially the irreversible capacity generated during the initial forming cycles, have attracted extensive attention. The initial irreversible capacity of carbonaceous materials has been well recognized as a critical point to the normal operation of Li-ion batteries. This irreversible capacity is known to result in the formation of a solid electrolyte interphase(SEI) film on the surface of carbonaceous anodes that effectively pre-

vents solvent decomposition and graphite exfoliation<sup>[4–7]</sup>. Similar SEI films on lithium transition metal oxide cathodes have been recently reported<sup>[8–10]</sup>. Studies of Fourier transform infrared spectroscopy(FTIRS)<sup>[8]</sup>, Raman spectroscopy, surface-enhanced Raman scattering(SERS)<sup>[9]</sup>, and X-ray photoelectron spectroscopy(XPS)<sup>[10]</sup> have demonstrated that the SEI film on the cathode is composed of various lithium salts, including lithium carbonate( $\text{Li}_2\text{CO}_3$ ), lithium alkoxides(ROLi), carboxylic lithium( $\text{RCO}_2\text{Li}$ ),  $\text{LiF}$ ,  $\text{Li}_x\text{PF}_y$ , and  $\text{PO}_x$  compounds.

$\text{LiMn}_2\text{O}_4$  is one of the most promising cathode materials to be used in Li-ion batteries because of its high theoretical energy density, high natural abundance, low cost, acceptable environmental characteristics, and good safety property. Unfortunately, it exhibits significant capacity fading during cycling<sup>[11–15]</sup>. It was reported<sup>[9]</sup> that the formation of the SEI film on spinel  $\text{LiMn}_2\text{O}_4$  electrodes involves a series of spontaneous reactions between the cathode active materials and the electrolyte solvents, and that the resulting film significantly reduces the electronic conductivity of the

\*Corresponding author. E-mail: [sgsun@xmu.edu.cn](mailto:sgsun@xmu.edu.cn)

Received September 27, 2007; accepted November 21, 2007.

Supported by the National Key Basic Research Program of China(No. 2002BC211804).

spinel  $\text{LiMn}_2\text{O}_4$  electrode and consequently causes capacity loss. However, little attention has been paid so far to the SEI film formed on the cathode, since its presence and importance on the performances of Li-ion batteries are not as well known as that of carbonaceous anodes.

To improve the energy density of Li-ion batteries, it is essential to understand and reduce the irreversible capacity of the cathode developed during the initial forming cycles. Therefore, in this study, we aimed at addressing surface-film formation, aging processes, and other phenomena that may be involved in the capacity-fading mechanism of the spinel  $\text{LiMn}_2\text{O}_4$  electrode. For this purpose, the formation process of the SEI film was studied by electrochemical impedance spectroscopy during the initial storage in 1 mol/L  $\text{LiPF}_6\text{-EC:DMC:DEC}$  electrolyte (only exposed to the electrolyte) and the subsequent first charge-discharge cycle.

## 2 Experimental

The stoichiometric compounds  $\text{LiMn}_2\text{O}_4$  were synthesized by solid-state reactions. The reagents  $\text{Li}_2\text{CO}_3$  and  $\text{MnO}_2$  were used as the starting materials. The mixtures were first heated at 300 °C for 2 h in air, and then the powders were ground until the homogeneous powders were obtained. The powders were continuously heated at 750 °C for 24 h in air and cooled down by simply switching off the electrical power. Finally, dark powders were obtained for measurement. The phase identification was carried out on a Rigaku D/max-rA diffractometer with  $\text{Cu } K\alpha$  radiation. Diffraction data were collected by step scanning over an angular range of 15°—70° with a step of 0.08°.

All electrochemical experiments were carried out in a three-electrode glass cell with Li foils as auxiliary and reference electrodes. The spinel  $\text{LiMn}_2\text{O}_4$  electrode used in this study was prepared by spreading a mixture of 80% active material, 3% acetylene black, 7% mesocarbon microbeads (Shanshan Co., Shanghai, China), and 10% poly(vinylidene difluoride) (PVdF, Kynar FLEX 2801, Elf-atochem, USA) binder dissolved in *N*-methyl pyrrolidone (Fluka Inc.) onto an aluminum foil current collector. The obtained electrode film was dried at 120 °C for 16 h under vacuum prior to use. The electrolyte was 1 mol/L  $\text{LiPF}_6\text{-EC:DMC:DEC}$  (volume ratio 1:1:1, Guotaihuarong Co., Zhangjiagang, China).

EIS measurements were conducted using an electrochemical working station (CHI 660B, Shanghai, China). The ac perturbation signal was 5 mV, the frequency ranged from  $10^5$  to  $10^{-2}$  Hz, and the electrodes were equilibrated for 1 h before measurement. The recorded EIS data were analyzed using Zview software.

## 3 Results and Discussion

### 3.1 Characterizations of XRD and Cyclic Voltammetry (CV)

The joint committee for powder diffraction standard (JCPDS) and the XRD patterns of  $\text{LiMn}_2\text{O}_4$  are shown in Fig. 1.

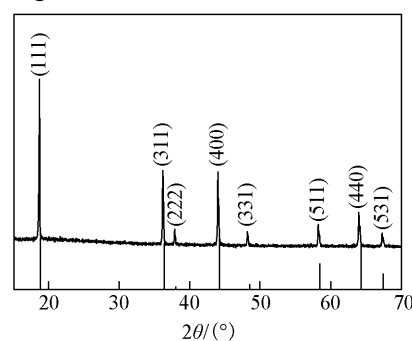


Fig. 1 JCPDS standard and XRD patterns of spinel  $\text{LiMn}_2\text{O}_4$  prepared by solid-state method

All patterns are in good agreement with the JCPDS standard, which can be indexed as cubic spinel phases.

Fig. 2 shows 7 successive cyclic voltammograms (CVs) recorded at 20  $\mu\text{V/s}$  for the spinel  $\text{LiMn}_2\text{O}_4$  electrode in 1 mol/L  $\text{LiPF}_6\text{-EC:DEC:DMC}$  electrolyte. Two anodic peaks at 4.18 and 4.05 V and two corresponding cathodic peaks at 4.06 and 3.95 V are the characteristics for the  $\text{LiMn}_2\text{O}_4$  electrode. As reported in the literatures<sup>[16,17]</sup>, the two pairs of peaks correspond to the two-step reversible (de)intercalation reaction, in which lithium ions occupy two different tetragonal 8a sites in spinel  $\text{Li}_x\text{Mn}_2\text{O}_4$  ( $0 < x < 1$ ).

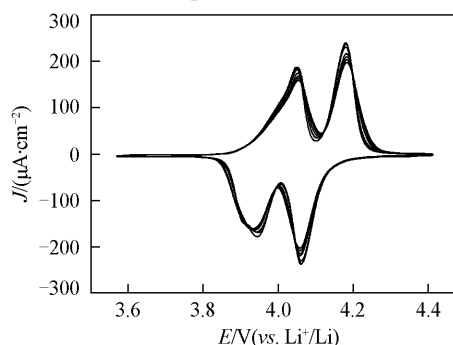
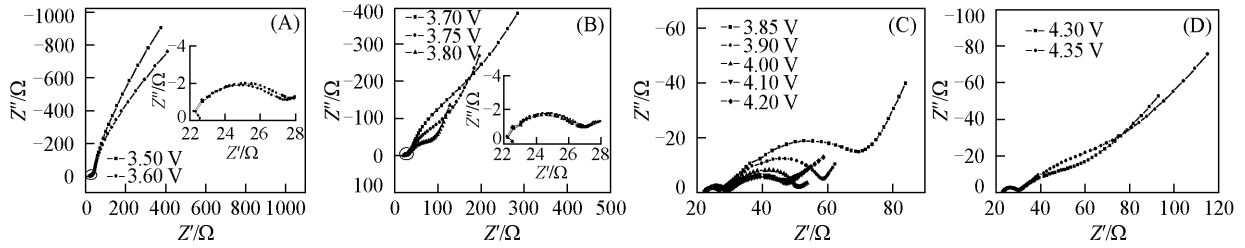


Fig. 2 Cyclic voltammogram recorded on the spinel  $\text{LiMn}_2\text{O}_4$  electrode at 20  $\mu\text{V/s}$

### 3.2 Common EIS Features of the Spinel $\text{LiMn}_2\text{O}_4$ Electrode

Typical electrochemical impedance spectra of the spinel  $\text{LiMn}_2\text{O}_4$  electrode at different potentials in the charge process are shown in Fig.3. The spectra at 3.5 and 3.6 V display a small arc in the high-frequency(HF) region( $f > 100$  Hz) and a slightly inclined line in the low-frequency(LF) region that represents the blocking character of the

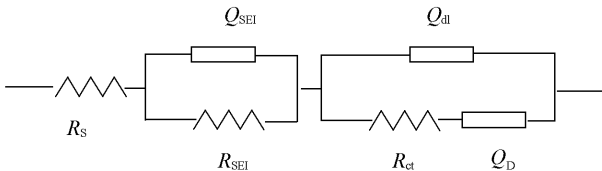


**Fig.3 Impedance spectra of spinel  $\text{LiMn}_2\text{O}_4$  electrode at different potentials in a frequency range of  $10^5-10^2$  Hz in the charge process**

The insets show the enlarged spectra over a  $10^5-10^2$  Hz frequency range.

### 3.3 Equivalent Circuits Proposed for EIS Analysis

Based on the experimental results, an equivalent circuit shown in Fig.4 is proposed to fit the EIS data of the storage and the subsequent first delithiation of the spinel  $\text{LiMn}_2\text{O}_4$  electrode. In the equivalent circuit,  $R_s$  represents the ohmic resistance;  $R_{\text{SEI}}$ , and  $R_{\text{ct}}$  are the resistances of the SEI film and the charge transfer reaction; the capacitance of the SEI film, the capacitance of the double layer, and the Warburg impedance are represented by the constant phase element(CPE)  $Q_{\text{SEI}}$ ,  $Q_{\text{dl}}$  and  $Q_{\text{D}}$ , respectively. The expression for the admittance response of CPE( $Q$ ) is:



**Fig.4 Equivalent circuit used for analysis of impedance spectra of spinel  $\text{LiMn}_2\text{O}_4$  electrode**

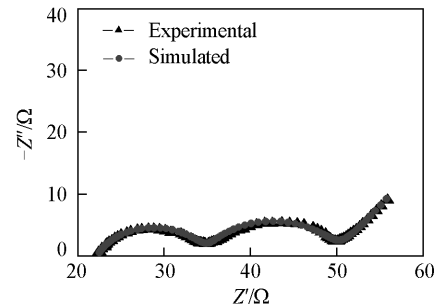
$$Y = Y_0 \omega^n \cos\left(\frac{n\pi}{2}\right) + j Y_0 \omega^n \sin\left(\frac{n\pi}{2}\right) \quad (1)$$

where,  $\omega$  is the angular frequency, and  $j$  is the imaginary unit. A CPE represents a resistor when  $n=0$ , a capacitor with a 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<sup>[20]</sup>.

In Fig.5, the simulated impedance spectrum is

non-delithiated electrode at equilibrium potential. The spectrum above 3.7 V gives rise to a similar HF arc as above and a second arc in the medium-frequency(MF) region followed by a straight line. According to Aurbach *et al.*<sup>[18,19]</sup>, the HF arc is related to SEI film( $R_{\text{SEI}}$  coupled with SEI film capacitance), the MF arc corresponds to charge transfer resistance coupled with double capacitance, and the straight line reflects the solid state Li-ion diffusion in the bulk of active mass.

compared with the EIS experimental data at 3.9 V during discharge process, and the values of parameters are listed in Table 1. It can be seen that the proposed model describes the experimental data satisfactorily.



**Fig.5 Comparison of EIS experimental data recorded at 3.9 V during discharge process with those obtained from simulation using equivalent circuit of Fig.4**

**Table 1 Equivalent circuit parameters obtained from Fig.5**

Parameter	Value	Uncertainty(%)
$R_s$	22.29	0.2752
$R_{\text{SEI}}$	12.64	1.181
$Q_{\text{SEI}}-n$	0.79072	1.1959
$Q_{\text{SEI}}-Y_0$	$4.0388 \times 10^{-5}$	8.8472
$R_{\text{ct}}$	14.92	1.8578
$Q_{\text{dl}}-n$	0.79358	1.6676
$Q_{\text{dl}}-Y_0$	$4.5674 \times 10^{-3}$	4.0428
$Q_{\text{D}}-n$	0.63303	2.9882
$Q_{\text{D}}-Y_0$	0.47294	5.7115
$\chi^2 = 5.15111 \times 10^{-4}$		

### 3.4 Storage Behavior of $\text{LiMn}_2\text{O}_4$ Electrode

Fig.6 illustrates the variations of different EIS parameters obtained by fitting experimental impe-

dance spectra of the spinel  $\text{LiMn}_2\text{O}_4$  electrode with increasing the storage time in 1 mol/L  $\text{LiPF}_6\text{-EC:DEC:DMC}$  electrolyte at open circuit potential. 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 Eqs.(2) and (3).

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

$$C = \varepsilon S / l \quad (3)$$

where,  $l$  denotes the thickness of SEI film,  $S$  denotes the electrode surface area,  $\rho$  denotes the resistivity, and  $\varepsilon$  denotes the permittivity of the SEI film. If we assume that the surface  $S$ , permittivity  $\varepsilon$ , and resistivity  $\rho$ , remain constant, it is clear that a thickness increase will lead to a resistance increase and a decrease

in capacitance. It can be seen from Fig.6 that both the resistance ( $R_{\text{SEI}}$ ) and the  $Q_{\text{SEI}-n}$  rapidly increase during the initial 4 h of the storage, whereas the pseudo capacitance ( $Q_{\text{SEI}-Y_0}$ ) quickly decreases. The changes of the parameters indicate that the SEI film has been formed on the spinel  $\text{LiMn}_2\text{O}_4$  electrode and its thickness increases rapidly during the initial 4 h of storage. In a prolonged storage process, the increase of  $R_{\text{SEI}}$  and the decrease of  $Q_{\text{SEI}-Y_0}$  both become slow, implying that spontaneous reactions occurring between the spinel  $\text{LiMn}_2\text{O}_4$  electrode and the electrolyte have been prevented by the SEI film.  $Q_{\text{SEI}-n}$  remains almost constant, confirming that the spinel  $\text{LiMn}_2\text{O}_4$  electrode is covered homogeneously by the SEI film.

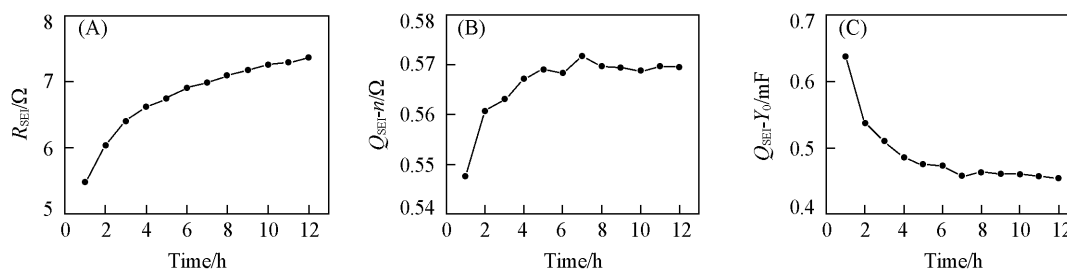


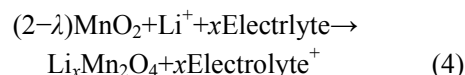
Fig.6 Variations of EIS parameters obtained from fitting the experimental impedance spectra of the spinel  $\text{LiMn}_2\text{O}_4$  electrode with the increase of storage time at open circuit potential(OCP, 3.5 V)

(A)  $R_{\text{SEI}}$ ; (B)  $Q_{\text{SEI}-n}$ ; (C)  $Q_{\text{SEI}-Y_0}$ .

### 3.5 EIS Studies of Spinel $\text{LiMn}_2\text{O}_4$ Electrode in the First Charge-discharge Cycle

The parameters obtained by fitting the experimental impedance spectra recorded in the first discharge-charge cycle subsequent to the storage are plotted in Fig.7. During the first charge process, the  $R_{\text{SEI}}$  decreases slightly below 3.95 V; this may be owing to the reversible breakdown(or dissolution) of the resistive SEI film<sup>[20]</sup>. It then increases in the potential range of (3.95—4.0) V, which may be ascribed to the decrease of surface electronic conductance of the  $\text{LiMn}_2\text{O}_4$  electrode caused by the phase transitions of delithiation. It remains invariant above 4.0 V until the end of the charge process, which is similar to that reported about the cycled  $\text{LiNiO}_2$  electrode<sup>[18]</sup>. It can be seen that the  $Q_{\text{SEI}-n}$  increases while the  $Q_{\text{SEI}-Y_0}$  decreases during the entire charge process, confirming the increase of the homogeneity and compactness of the SEI film. At the end of the discharge process, the electrode potential was kept at 4.35 V for 12 h; both the  $R_{\text{SEI}}$  and  $Q_{\text{SEI}-n}$  increased considerably, but the  $Q_{\text{SEI}-Y_0}$  decreased slightly, indicating the thickening of the SEI film owing to electrolyte oxidation. In the

succeeding discharge process, the changes of  $R_{\text{SEI}}$ ,  $Q_{\text{SEI}-n}$ , and  $Q_{\text{SEI}-Y_0}$  with decreasing polarization potential are similar to that in the charge process before the lithiation of the  $\text{LiMn}_2\text{O}_4$  electrode(4.2 V, as can be seen from the CV). When Li-ion begins to insert into the  $\text{LiMn}_2\text{O}_4$  electrode, the  $R_{\text{SEI}}$  increases rapidly and  $Q_{\text{SEI}-Y_0}$  increases slightly with the decrease of the polarization potential, signifying the increase of the thickness of the SEI film; the  $Q_{\text{SEI}-n}$  decreases, denoting the decrease of homogeneity of the SEI film. We consider that the behavior may be associated to electrolyte oxidation coupled with Li-ion insertion, as suggested by Eriksson *et al.*<sup>[21]</sup>.



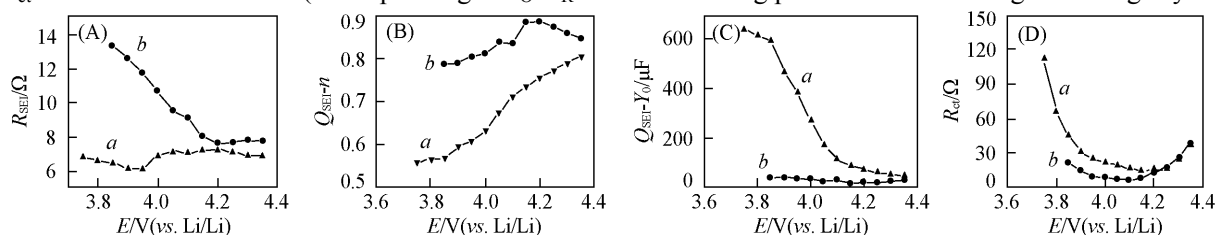
The  $R_{\text{ct}}$  versus  $E$  plot, is supposed to perform according to the following classical equation<sup>[22]</sup>:

$$R_{\text{ct}} = 1 / f F k_0 A c_{\text{O}}^{0.5} c_{\text{R}}^{0.5} \quad (5)$$

In equation (5),  $f$  denotes the usual electrochemical constant(equal to  $F/RT$ , where,  $F$  and  $R$  are Faraday and gas constant, respectively, and  $T$  is the absolute temperature) and  $k_0$  is the heterogeneous rate constant, respectively. It should be remembered that when Eq.(5) is used, the total concentration of the

available intercalation sites,  $c_T$ , is constant, *i.e.*,  $c_O + c_R = c_T$ . The concentrations of the red-form,  $c_R$ , and that of the ox-form,  $c_O$ , are identified with the concentration of Li ions and unoccupied intercalation sites, respectively.

Eq.(5) clearly predicts a rapid increase in  $R_{ct}$  as  $c_O \rightarrow c_T$  or  $c_R \rightarrow c_T$ , *i.e.*, in either completely intercalated or deintercalated state, the minimum  $R_{ct}$  can be attained when  $c_O = c_R$ . It can be observed from Fig.6 that the  $R_{ct}$  decreases below 4.15 V (corresponding to  $c_O = c_R$



**Fig.7 Variations of EIS parameters with electrode potential obtained from fitting the experimental impedance spectra of the spinel  $LiMn_2O_4$  electrode during the first charge-discharge cycle**

(A)  $R_{SEI}$ ; (B)  $Q_{SEI-n}$ ; (C)  $Q_{SEI-Y_0}$ ; (D)  $R_{ct}$ . a. Charge; b. discharge.

## 4 Conclusions

The initial storage in electrolyte and the subsequent first charge-discharge cycle of the spinel  $LiMn_2O_4$  electrode were studied by EIS. The results demonstrate that the thickness of the SEI film increases with increasing the storage time for the spinel  $LiMn_2O_4$  electrode in 1 mol/L  $LiPF_6$ -EC:DEC:DMC electrolyte, and spontaneous reactions of the spinel  $LiMn_2O_4$  electrode with electrolyte can be prevented by the SEI film. In the first charge-discharge cycle subsequent to the storage, the reversible breakdown (or dissolution) of the resistive SEI film leads to the decrease of the  $R_{SEI}$ , and the decrease of surface electronic conductance of the  $LiMn_2O_4$  electrode as well as the electrolyte oxidation result in the increase of the  $R_{SEI}$  in the charge process; however, the electrolyte oxidation coupled with Li-ion insertion has been illustrated as the main origin for the increase of resistance of the SEI film in the whole charge-discharge process. The results have demonstrated that a classical equation can be used to describe the variations of the  $R_{ct}$  with potential.

## References

- [1] Nagaura T., Tazawa K., *Prog. Batteries Sol. Cells*, **1990**, 9, 20
- [2] Scrosati B., *J. Electrochem. Soc.*, **1992**, 139, 10
- [3] Zhang X., Ross P. N., Kostecki Jr. R., *et al.*, *J. Electrochem. Soc.*, **2001**, 148, A463
- [4] Peled E., Golodnitsky D., Ardel G., *J. Electrochem. Soc.*, **1997**, 144, L208
- [5] Aurbach D., Zaban A., *J. Electroanal. Chem.*, **1993**, 348, 155
- [6] Ein-Eli Y., *Electrochem. Solid-State Lett.*, **1999**, 2, 212
- [7] Zhang S. S., Ding M. S., Xu K., *et al.*, *Electrochem. Solid-State Lett.*, **2001**, 4, A206
- [8] Aurbach D., Levi M. D., Levi E., *et al.*, *J. Electrochem. Soc.*, **1998**, 145, 3024
- [9] Matsuo Y., Kostecki R., McLarnon F., *J. Electrochem. Soc.*, **2001**, 148, A687
- [10] Edström K., Gustafsson T., Thomas J. O., *Electrochimica Acta*, **2004**, 50, 397
- [11] Yamada A., Tanaka M., *Mater. Res. Bull.*, **1995**, 30, 715
- [12] Xia Y., Zhou Y., Yoshio M., *J. Electrochem. Soc.*, **1997**, 144, 2593
- [13] Jang D. H., Shin Y. J., Oh S. M., *J. Electrochem. Soc.*, **1996**, 143, 2204
- [14] Thackeray M. M., Shao-Horn Y., Kahaian A. J., *et al.*, *Electrochem. Solid-State Lett.*, **1998**, 1, 7
- [15] Huang H., Vincent C. A., Bruce P. G., *J. Electrochem. Soc.*, **1999**, 146, 481
- [16] Thackeray M. M., David W. I. F., Bruce P. G., *et al.*, *Mater. Res. Bull.*, **1983**, 18, 461
- [17] Miura K., Yamada A., Tanaka M., *Electrochim. Acta*, **1996**, 41, 249
- [18] Aurbach D., Gamolsky K., Markovsky B., *et al.*, *J. Electrochem. Soc.*, **2000**, 147, 1322
- [19] Aurbach D., Levi M. D., Gamulski K., *et al.*, *J. Power Source*, **1999**, 81/82, 472
- [20] Kim Y. O., Park S. M., *J. Electrochem. Soc.*, **2001**, 148, A194
- [21] Eriksson T., Andrsson A. M., Gejke C., *et al.*, *Langmuir*, **2002**, 18, 3609
- [22] Levi M. D., Gamosky K., Aurbach D., *et al.*, *Electrochimica Acta*, **2000**, 45, 1781