



Polyimide gel polymer electrolyte-nanoencapsulated LiCoO₂ cathode materials for high-voltage Li-ion batteries

Jang-Hoon Park^a, Jong-Su Kim^b, Eun-Gi Shim^b, Kyung-Won Park^c, Young Taik Hong^d, Yun-Sung Lee^{e,*}, Sang-Young Lee^{a,*}

^a Department of Chemical Engineering, College of Engineering, Kangwon National University, Chuncheon, Kangwondo, 200-701, Korea

^b Techno Semichem, Yongin, Gyeonggi-do, 446-599, Korea

^c Department of Chemical and Environmental Engineering, Soongsil University, Seoul, 156-743, Korea

^d Energy Materials Research Center, Korea Research Institute of Chemical Technology, Yuseong, Daejeon 305-600, Korea

^e School of Applied Chemical Engineering, Chonnam National University, Gwangju, 500-757, Korea

ARTICLE INFO

Article history:

Received 29 March 2010

Received in revised form 21 May 2010

Accepted 27 May 2010

Available online 2 June 2010

Keywords:

Lithium-ion batteries

LiCoO₂

High-voltage

Nanoencapsulation

Polyimide

Interfacial reaction

ABSTRACT

We demonstrate a novel and facile approach to surface modification of high-voltage charged LiCoO₂, which is based on encapsulating LiCoO₂ by a polyimide (PI) gel polymer electrolyte layer. The PI is introduced onto the LiCoO₂ by thermally curing 4-component (pyromellitic dianhydride/biphenyl dianhydride/phenylenediamine/oxydianiline) polyamic acid. The PI nanoencapsulating layer features the high surface coverage, nanometer thickness, and facile ion transport. These unique characteristics are expected to enable the PI coating layer to effectively suppress the undesirable interfacial reaction of the LiCoO₂ with liquid electrolyte, which plays a key role in noticeably improving the 4.4 V cycle performance and mitigating the vigorous exothermic reaction between the charged LiCoO₂ and liquid electrolyte.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Rapidly growing demands for higher energy-density lithium-ion batteries continue to stimulate research and development for a new cathode material capable of delivering large reversible capacity [1–3]. LiCoO₂ is currently one of the most popular cathode materials in commercial lithium-ion batteries due to the ease of preparation, good C-rate capability, and excellent cycle performance. Charging the LiCoO₂ cathode above 4.2 V has been proposed as an effective way to increase its reversible capacity [4–6]. However, the corresponding increase of impedance between the LiCoO₂ and liquid electrolyte with increasing the upper cut-off voltage poses the serious problems with capacity fading during the cell cycle [5–9]. In order to improve the electrochemical performance of high-voltage charged LiCoO₂, coating LiCoO₂ with metal oxides such as Al₂O₃, ZrO₂, MgO, and ZnO has been extensively investigated [9–12]. However, metal oxides, often

discontinuously deposited onto LiCoO₂, tend to act as an inert layer to ionic conduction, and require complex and cost-consuming coating processes.

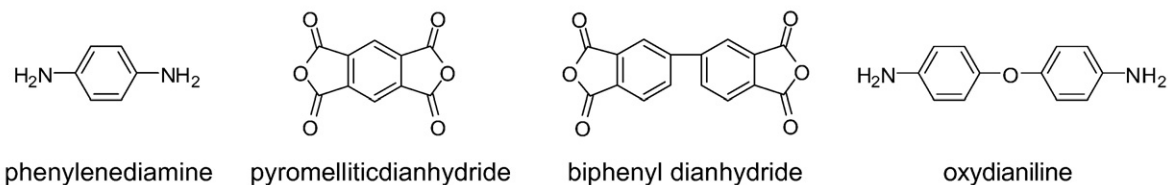
These limitations motivate us to demonstrate a novel and facile approach to the surface modification of LiCoO₂, which is based on encapsulating LiCoO₂ by a nanometer-thickness gel polymer electrolyte (GPE) layer. Judging from the extent of surface coverage onto LiCoO₂ and the feasibility of lithium-ion transport, a GPE is possibly expected to be promising, because it may easily form a continuous, lithium-ion conducting coating layer. In this study, polyimide (PI) is employed as a representative example of GPE coating layers. The PI is synthesized by thermally curing 4-component (pyromellitic dianhydride/biphenyl dianhydride/phenylenediamine/oxydianiline) polyamic acid onto LiCoO₂. PI has been widely used in various applications such as microelectronics, displays, membranes, and fuel cells, owing to its well-balanced chemical and mechanical stability in addition to outstanding film-forming properties [13–16]. Therefore, PI is expected to be suitable for forming the encapsulating layer of LiCoO₂. The thermally-cured PI fulfills the critical requirement that it must be insoluble in N-methyl pyrrolidone, a common solvent used during cathode fabrication. The performance of PI-nanoencapsulated LiCoO₂ is investigated in terms of cyclability and thermal stability of high-voltage (4.4 V) charged cells.

* Corresponding authors. S.-Y. Lee is to be contacted at tel.: +82 33 250 6338; fax: +82 33 251 3658; Y.-S. Lee, tel.: +82 62 530 1904; fax: +82 62 530 1909.

E-mail addresses: leey@chonnam.ac.kr (Y.-S. Lee), syleek@kangwon.ac.kr (S.-Y. Lee).

2. Experimental

The chemical structure of the each component in the polyamic acid is given below.



The 4-component polyamic acid solution was prepared using dimethylacetamide as a solvent. The detailed synthesis on the polyamic acid has been described in previous publications [15,16]. The concentration of polyamic acid in the solution was fixed at 5 wt.%. LiCoO_2 powders (average particle size = 10 μm , Umicore) were added in the coating solutions and stirred for 10 min, then filtered. The filtered powders were dried at 30 $^\circ\text{C}$ for 1 h and further vacuum-dried at 30 $^\circ\text{C}$ for 4 h. Meanwhile, in order to convert the polyamic acid into the PI, the polyamic acid-coated LiCoO_2 powders were thermally imidized via a stepwise imidization process (60 $^\circ\text{C}$ for 30 min \rightarrow 120 $^\circ\text{C}$ for 30 min \rightarrow 200 $^\circ\text{C}$ for 60 min \rightarrow 300 $^\circ\text{C}$ for 60 min \rightarrow 400 $^\circ\text{C}$ for 10 min) under nitrogen atmosphere. The imidization reaction was confirmed using FT-IR (FT-3000, Excalibur) by measuring the characteristic peaks assigned to the imide ring of the PI coating layer. A LiCoO_2 cathode was prepared by coating NMP-based slurry with a mixture of 95 wt.% of LiCoO_2 , 3 wt.% of polyvinylidene fluoride (PVdF) binder, and 2 wt.% of carbon black on an aluminum current collector. The surface morphology of the PI-coated LiCoO_2 was examined using FE-SEM (S-4300, Hitachi) and TEM (Tecnai G2 F30, FEI). A unit cell (2032 coin) was assembled by sandwiching a PE separator (thickness = 20 μm) between a natural graphite anode and the surface-modified LiCoO_2 cathode. It was activated by filling with a liquid electrolyte of 1 M LiPF_6 in ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (= 1/2 v/v). The discharge capacities of cells were examined as a function of discharge current density using a cycle tester (PNE Solution). The discharge current densities between 0.2 C (= 0.59 mA cm^{-2}) and 2.0 C (= 5.87 mA cm^{-2}) were employed at a constant charge current density of 0.2 C under a voltage range

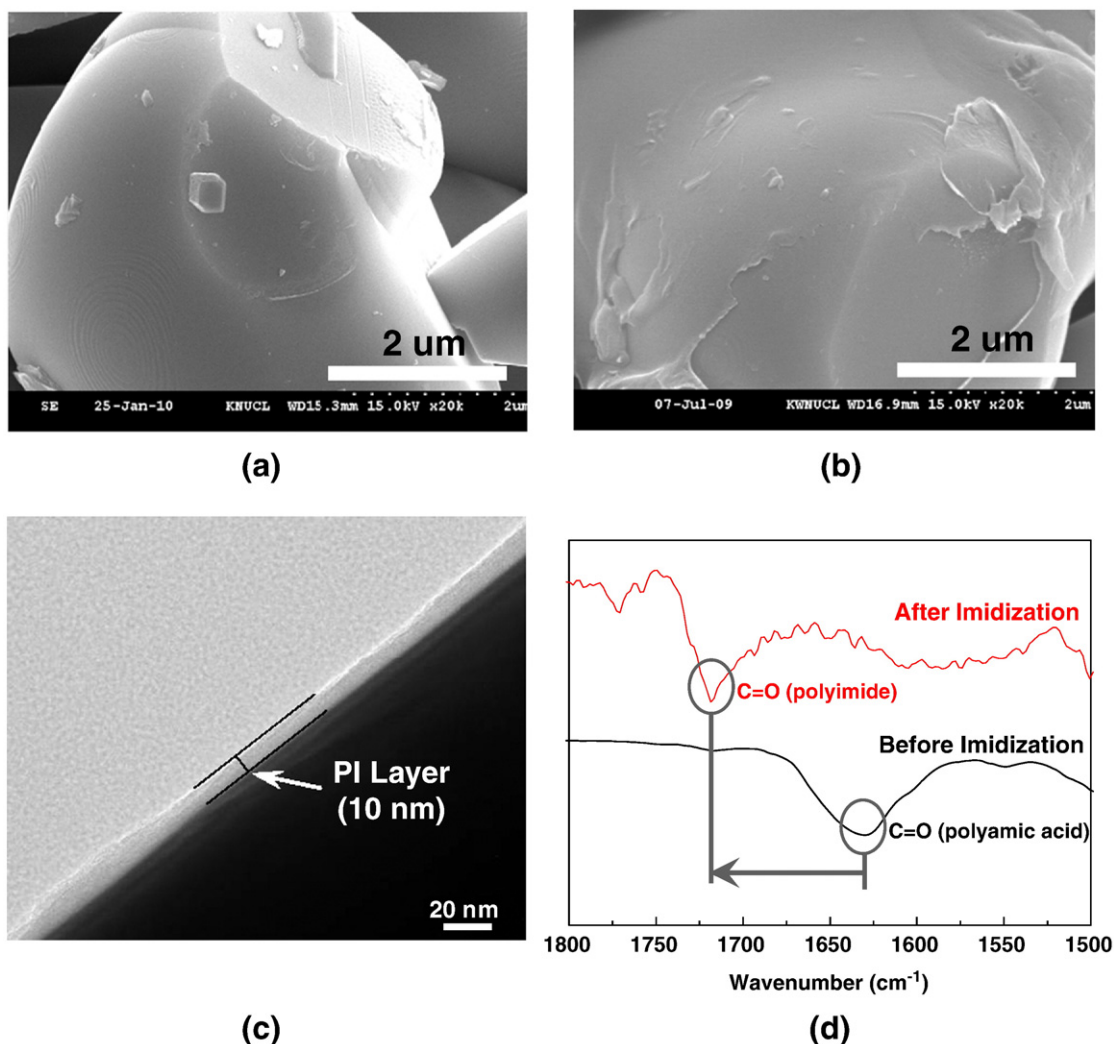


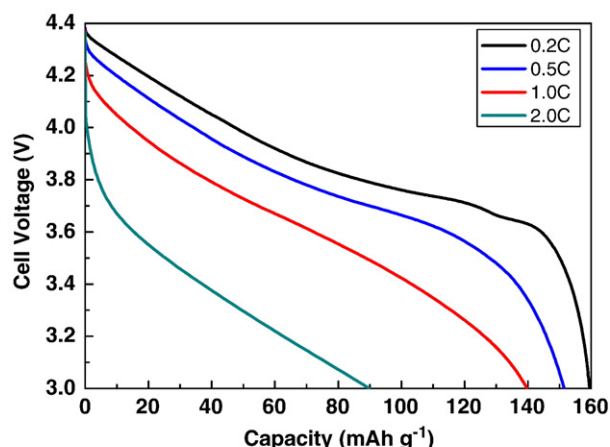
Fig. 1. FE-SEM photographs of (a) pristine LiCoO_2 ; (b) PI-coated LiCoO_2 ; (c) TEM photograph of PI-coated LiCoO_2 ; and (d) IR spectra of PI-coated LiCoO_2 .

of 3.0 V–4.4 V. The cells were cycled at a constant charge/discharge current density of 0.5 C/0.5 C. The AC impedance of cells was measured using a VSP classic (Bio-Logic) over a frequency range of 0.01 Hz to 10^6 Hz. The exothermic reaction between the charged cathode and liquid electrolyte was examined by DSC (DuPont Q2000) measurements, where the cells were charged to 4.4 V at a current density of 0.2 C and then disassembled in a dry room to remove the charged cathode. The DSC measurements were performed at a heating rate of $10^\circ\text{C min}^{-1}$.

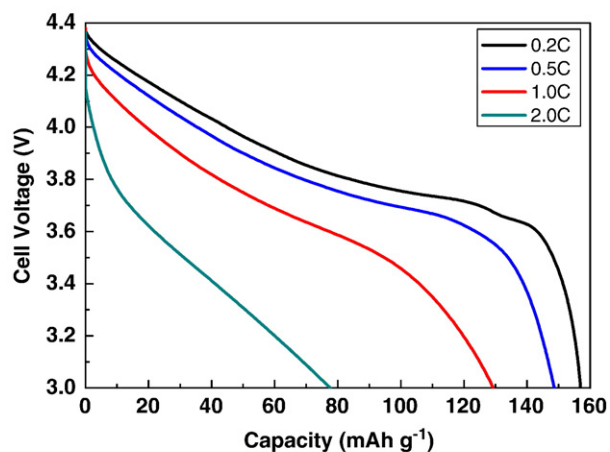
3. Results and discussion

The surface morphology of PI-coated LiCoO_2 is compared with that of pristine one. Fig. 1 shows the successful encapsulation of the LiCoO_2 with the PI coating layer. Onto the surface of LiCoO_2 , the PI forms a smooth and continuous coating layer with a thickness of around 10 nm (Fig. 1(c)). The polyamic acid's polarity [17] may allow its strong affinity for LiCoO_2 . This intimate contact of the polyamic acid with LiCoO_2 , in addition to its excellent film-forming properties [13–16], may contribute to its high surface coverage. The existence of PI onto the LiCoO_2 is further confirmed by the FT-IR analysis (Fig. 1(d)). The peak assigned to the C=O bond of the PI coating layer is observed at 1723 cm^{-1} , whereas the starting polyamic acid shows the peak for the C=O bond at 1630 cm^{-1} .

Fig. 2 demonstrates the effect of PI coating layer on the discharge profiles of cells charged to 4.4 V. The pristine LiCoO_2 shows a conventional voltage plateau and a high discharge capacity of 160 mAh g^{-1} at a discharge current density of 0.2 C. The discharge capacities of the PI-coated LiCoO_2 are found to be comparable to those of the pristine LiCoO_2 , although they are marginally lower at higher discharge current densities. As the PI coating layer has the continuous

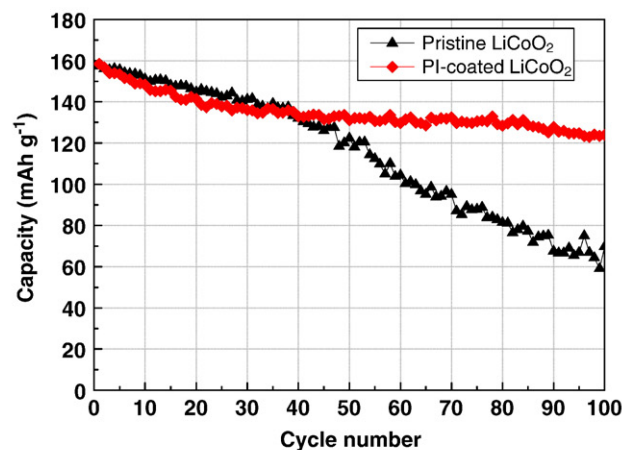


(a)

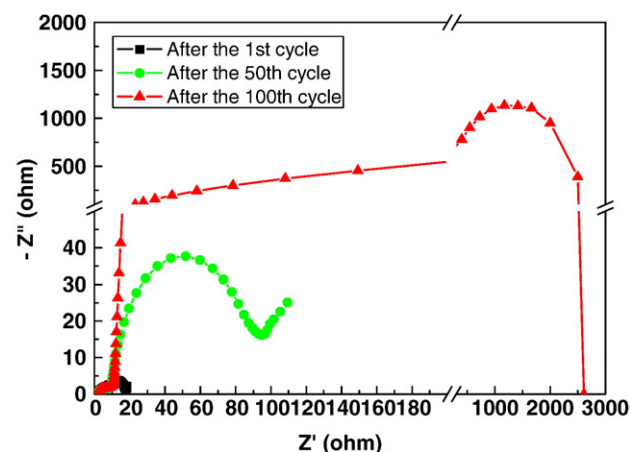


(b)

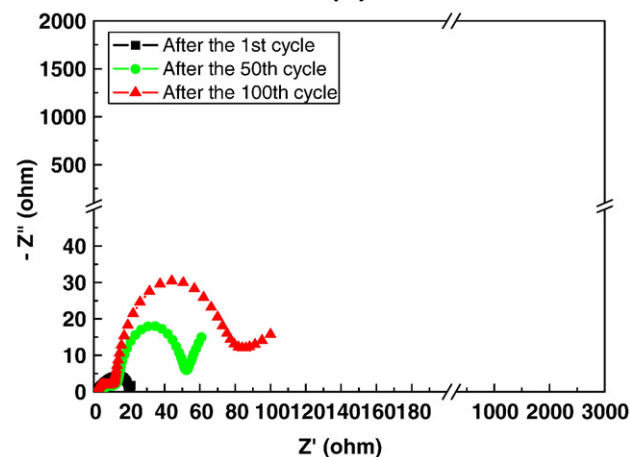
Fig. 2. Discharge profiles of cells charged to 4.4 V as a function of C-rate: (a) pristine LiCoO_2 ; and (b) PI-coated LiCoO_2 .



(a)



(b)



(c)

Fig. 3. (a) Discharge capacities as a function of cycle number for cells assembled with pristine LiCoO_2 or PI-coated LiCoO_2 ; AC impedance spectra of cells after the 1st, 50th, and 100th cycle: (b) pristine LiCoO_2 ; and (c) PI-coated LiCoO_2 .

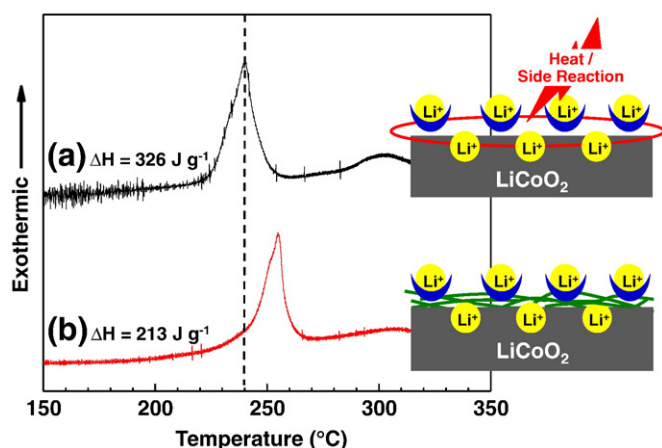


Fig. 4. DSC thermograms of exothermic reaction between 4.4 V-charged LiCoO_2 and liquid electrolyte and schematic representation illustrating interfacial reaction: (a) pristine LiCoO_2 ; and (b) PI-coated LiCoO_2 .

coverage of nanometer thickness, ion transport in the PI coating layer is likely not to be significantly hindered. The supplement experiment shows that the PI film swelled with liquid electrolyte has an excellent ionic conductivity of 0.15 mS cm^{-1} . Therefore, the facile ion transport and unique structure of the PI coating layer could contribute to delivering the satisfactory discharge capacities.

Fig. 3(a) shows the effect of PI-coated LiCoO_2 on the cycle performance, i.e. discharge capacity as a function of cycle number, of cells charged to 4.4 V. Compared to the pristine LiCoO_2 , the PI-coated LiCoO_2 exhibits the significantly improved cycle performance. In the first 40 cycles, there is little difference between the pristine LiCoO_2 and the PI-coated one. However, after 40 cycles, the capacity fading of the PI-coated LiCoO_2 is heavily retarded, whereas the capacity of the pristine LiCoO_2 continues to drop with increasing cycle number. The capacity retention after 100 cycles is found to be 38% for the pristine LiCoO_2 and 76% for the PI-coated LiCoO_2 . In order to better understand the improved cyclability of the PI-coated LiCoO_2 , the AC impedance spectra of the charged cells after the 1st, 50th, and 100th cycle are analyzed. It has been known [5–7] that the semicircle in the high frequency range is ascribed to the resistance of surface film on the electrode active particles and the semicircle observed at medium-to-low frequency region is attributed to the charge transfer resistance between the electrode active particles and liquid electrolyte. Fig. 3(b) shows that the charge transfer resistance of the pristine LiCoO_2 significantly increases after the 100th cycle. This reveals that the sharp capacity fading of the pristine LiCoO_2 (Fig. 3(a)) could be associated with the undesirable interfacial reaction between the charged LiCoO_2 surface and liquid electrolyte. Previous studies [5–12] reported that predominantly due to the liquid electrolyte decomposition at high voltage, a resistive layer could be formed on the electrode particle surface. The resistive layer may hinder charge transport at the electrode active particles/liquid electrolyte interface, which consequently deteriorates cycle performance of a high-voltage charged cell. In comparison to the pristine LiCoO_2 , the PI-coated LiCoO_2 presents the slightly increased charge transfer resistance during the 4.4 V cycling (Fig. 3(c)). This demonstrates that the PI coating layer can effectively suppress the formation of a resistive layer onto the LiCoO_2 surface.

Fig. 4 compares the DSC thermograms of pristine LiCoO_2 and PI-coated LiCoO_2 charged to 4.4 V. The pristine LiCoO_2 shows a large exothermic heat ($\Delta H = 326 \text{ J g}^{-1}$) and an exothermic peak temperature of 239°C , which is due to the vigorous interfacial reaction of the charged LiCoO_2 with liquid electrolyte [6,7,12]. On the other hand, for the PI-coated LiCoO_2 , the exothermic heat is noticeably reduced ($\Delta H = 213 \text{ J g}^{-1}$) and the exothermic peak is also shifted to a high temperature of 255°C . This indicates that the PI coating layers are effective in mitigating the exothermic reaction between the charged LiCoO_2 and liquid electrolyte. Schematic illustrations for this interesting behavior of the PI-coated LiCoO_2 are also shown in Fig. 4. The high surface coverage of the PI coating layer is believed to play an important role in preventing the LiCoO_2 from being exposed directly to the reactive liquid electrolyte, thus lessening the exothermic reaction.

4. Conclusion

The high-voltage (4.4 V) cell performance and thermal stability of LiCoO_2 have been remarkably improved by the thermally-cured PI nanoencapsulating layer. The PI coating layer features high surface coverage, nanometer thickness, and facile ion transport. These unique characteristics enabled the PI layer to effectively suppress the undesirable interfacial reaction of the LiCoO_2 with liquid electrolyte, which contributed to improving the 4.4 V cycle performance and mitigating the exothermic reaction between the charged LiCoO_2 and liquid electrolyte. In future studies, the PI-coated LiCoO_2 charged to various cut-off voltages will be examined and the chemical structures of PI coating layers will be also optimized.

Acknowledgment

This work was supported by the IT R&D program of MKE/KEIT [K1002176-2010-02, Development of 3.6Ah Class Cylindrical Type Lithium Secondary Battery].

References

- [1] J.M. Tarascon, M. Armand, *Nature* 414 (2001) 359.
- [2] J. Thomas, *Nat. Mater.* 2 (2003) 705.
- [3] M.S. Whittingham, *Chem. Rev.* 104 (2004) 4271.
- [4] A. Abouimrane, I. Belharouak, K. Amine, *Electrochem. Comm.* 11 (2009) 1073.
- [5] K.S. Lee, Y.K. Sun, J. Noh, K.S. Song, D.W. Kim, *Electrochem. Comm.* 11 (2009) 1900.
- [6] Y.K. Sun, J.M. Han, S.T. Myung, S.W. Lee, K. Amine, *Electrochem. Comm.* 8 (2006) 821.
- [7] Y.K. Sun, S.W. Cho, S.T. Myung, K. Amine, J. Prakash, *Electrochim. Acta* 53 (2007) 1013.
- [8] D. Aurbach, B. Markovsky, A. Rodkin, E. Levi, Y.S. Cohen, H.J. Kim, M. Schmidt, *Electrochim. Acta* 47 (2002) 4291.
- [9] H. Miyashiro, A. Yamanka, M. Tabuchi, S. Seki, M. Nakayama, Y. Ohno, Y. Kobayashi, Y. Mita, A. Usami, M. Wakihara, *J. Electrochem. Soc.* 153 (2006) A348.
- [10] Z. Chen, J.R. Dahn, *Electrochim. Acta* 49 (2004) 1079.
- [11] Z. Chen, J.R. Dahn, *Electrochem. Solid State Lett.* 5 (2002) A213.
- [12] W. Chang, J.W. Choi, J.C. Im, J.K. Lee, *J. Power Sources* 195 (2010) 320.
- [13] Y.K. Lee, J.D. Craig, *Polymer Materials for Electronic Applications* 9 (1982) 107.
- [14] W. Essafi, G. Gebel, R. Mercier, *Macromolecules* 37 (2004) 1431.
- [15] H.C. Liou, P.S. Ho, R. Stierman, *Thin Solid Films* 339 (1999) 68.
- [16] L.Y. Jiang, Y. Wang, T.S. Chung, X.Y. Qiao, J.Y. Lai, *Progress in Polymer Science* 34 (2009) 1135.
- [17] J. Brandrup, E.H. Immergut, *Polymer handbook*, 3rd edition John Wiley & Sons, New York, 1989.