Journal of Electrochemical Science and Technology
Vol. 2, No. 1, 2011, 8-13
DOI:10.5229/JECST.2011.2.1.008

Journal of Electrochemical Science and Technology

Cycling Performance and Surface Chemistry of Si-Cu Anode in Ionic Liquid Battery Electrolyte Diluted with Dimethyl Carbonate

Cao Cuong Nguyen[a], Dong-Won Kim[b] and Seung-Wan Song[a,†]
[a]*Department of Fine Chemical Engineering & Applied Chemistry, Chungnam National University, Daejeon, 305–764, South Korea*
[b]*Department of Chemical Engineering, Hanyang University, Seoul, 133–791, South Korea*

ABSTRACT :

Interfacial compatibility between the Si-Cu electrode and diluted ionic liquid electrolyte containing 50 vol.% of 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)/1-methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide (MPP–TFSI) and 50 vol.% dimethyl carbonate (DMC) in a lithium cell and dilution effect on surface chemistry are examined. *ex-situ* ATR FTIR analysis results reveal that the surface of the Si-Cu electrode cycled in the diluted ionic liquid electrolyte is effectively passivated with the SEI layer mainly composed of carboxylate salts-containing polymeric compounds produced by the decomposition of DMC. Surface species by the decomposition of TFSI anion and MPP cation are found to be relatively in a very low concentration level. Passivation of electrode surface with the SEI species contributes to protect from further interfacial reactions and to preserve the electrode structure over 200 cycles, delivering discharge capacity of > 1670 mAhg^{-1} and capacity retention of 88% of maximum discharge capacity.

Keywords : Rechargeable lithium batteries, Si-based anode, Diluted ionic liquid electrolyte, SEI layer

Received December 17, 2010 : Accepted January 22, 2011

1. Introduction

Rechargeable lithium batteries are being widely used in ranged from portable electronic devices to hybrid electric vehicles to large scale energy storage systems (ESS).[1)] Scaling-up of rechargeable lithium batteries toward electric vehicle and large format ESS demands the development of higher energy density electrode materials with a stable cycling ability than conventional ones. Silicon (Si)-based materials have received a particular attention as alternative anode materials to graphite, due to the high theoretical capacity of Si of 3579 mAhg^{-1} for $Li_{15}Si_4$ at room temperature.[2)] Severe volume change of Si anode during lithiation and delithiation however results in electrochemical and mechanical disintegration, and rapid capacity fade.[2,3)] Cycling performance of the Si anode could be improved by controlling crystallinity[4,5)] and nanostructure of Si.[6)] Interfacial reaction between Si-based anodes and electrolyte and the solid electrolyte interphase (SEI) composition have been noticed as another causes responsible for cycling performance.[7,8)]

Room temperature ionic liquids have been intensively studied as alternative electrolyte materials for rechargeable lithium batteries because of their non-flammability, and high electrochemical and thermal stabilities.[9,10)] Our earlier works revealed that amorphous Si-Cu anode cycled excellently in 1-methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide(MPP-TFSI) - based ionic liquid electrolyte.[8)] A stable SEI layer was found to be formed on the Si-Cu anode, which composed of organic and inorganic compounds decomposed from MPP cations and TFSI anions, respectively, and/or their radical combinations. Passivation of the anode surface resulted in improved initial cycling efficiency and capacity retention as well.[8)] Nonetheless, the high viscosity of ~63 cP and low ionic

---

[†]Corresponding author. Tel.: +82-42-821-7008
E-mail address: swsong@cnu.ac.kr

conductivity ~1.4 $mScm^{-1}$ of the MPP-TFSI ionic liquid,[9] compared to carbonate-based organic solvents (e.g. ~1.3 cP and 8.2 $mScm^{-1}$ for EC : DEC (1 : 1 volume ratio))[11] used in the conventional electrolyte, are still barriers to overcome for a practical use in room temperature and lower temperature batteries.[10] Dilution of the 1 M LiTFSI/MPP-TFSI ionic liquid electrolyte with carbonate-based organic solvent (e.g. ~0.6 cP and 7.1 $mScm^{-1}$ for DMC[11]) can lower down viscosity and increase ionic conductivity. Given that the lowest proportion of ionic liquid in diluted ionic liquid electrolyte for suppressing flammability is 40 volume percent (vol.%),[12] and optimum viscosity and ionic conductivity of ionic liquid electrolyte are obtained with the concentration of lithium salt in between 0.4 and 0.6 M,[11] the dilution of the ionic liquid electrolyte with 50 vol% DMC is best considered for obtaining 0.5 M LiTFSI-containing diluted electrolyte.

In this work, we present the electrochemical behavior and surface chemistry of the Si-Cu anode in the diluted ionic liquid electrolyte of 0.5 M LiTFSI/MPP-TFSI : DMC (50 : 50 vol%), with an emphasis on *ex-situ* attenuated total reflection (ATR) FTIR spectroscopic surface characterization.

2. Experimental

Films of the Si-Cu were deposited on Cu substrates by pulsed laser deposition at 200°C in 5 mTorr of Ar back pressure, using KrF excimer laser with an energy density of ~3-4 $mJcm^{-2}$ at 10 Hz impinging on a Si-Cu target with 10 mol% Cu. The thickness of the film was observed as 60 nm by a field emission scanning electron microscope (FE SEM, Sirion) at 5 kV. The atomic ratio of Si : Cu film was 89 : 11 in mol%, determined using X-ray photoelectron spectroscopy depth profile (Thermo, MultiLab 2000) with Al K_α X-ray source and Ar-ion sputtering at 2 kV. The surface morphology and the elemental mapping of the Si and Cu over the as-deposited film were observed using SEM (FESEM, JEOL JSM-7000F). The structure of the as-deposited Si-Cu film was characterized by X-ray diffraction (Rigaku D/MAX-2200) and Raman spectroscopy (Tokyo instrument Co., Nanofinder 30).

Electrochemical behavior of the Si-Cu film electrode was evaluated using three electrode lithium cells with the Si-Cu electrode as working electrode, lithium reference and counter electrodes in 1 M $LiPF_6$/ethylene carbonate (EC) : diethyl carbonate (DEC) (3 : 7 volume ratio) (Techno Semichem) and diluted ionic liquid electrolyte of 0.5 M LiTFSI/MPP-TFSI:DMC (1 : 1 volume ratio). Diluted ionic liquid electrolyte of 0.5 M LiTFSI/MPP-TFSI : DMC was prepared by mixing equal volume of 1 M LiTFSI (99.95 %, Aldrich)/MPP-TFSI (> 99%, Citri) and DMC (Techno Semichem). Prior to the preparation of ionic liquid electrolyte, the MPP-TFSI and LiTFSI were dried in vacuum oven at 110°C for 48 hrs for the removal of water. Galvanostatic cycling was conducted in the voltage region of 0.1-1.5 V *vs.* Li/Li^+ at 35 μAcm^{-2}, which corresponds to ~2.5 Ag^{-1}, using a multichannel cycler (Wonatech). For *ex-situ* FTIR analysis, the cycled electrodes were carefully separated from the cells and washed with DMC for 20s for the removal of residual electrolyte followed by drying in the Ar-filled glove box at room temperature. Electrolyte preparation, cell assembly and electrochemical testing were carried out in the glove box (MO Tek) with oxygen and water contents below 1 ppm.

Surface characterization of the cycled electrodes was performed using *ex-situ* ATR FTIR spectroscopy using an IR spectrometer (Bruker optics IFS66V/S) equipped with a mercury-cadmium-telluride detector. To avoid exposure of samples to air during sample transportation from glove box to IR instrument as well as during IR measurement, the cycled electrodes were directly mounted on the tightly closed single-reflection ATR unit with a Ge optic in the glove box. Spectral resolution was 4 cm^{-1} and a total of 512 scans were co-added.

3. Results and Discussions

3.1. Characterization of the as-deposited Si-Cu electrode

The surface of the as-deposited Si-Cu film appears rough, covered by the particles with ~40 nm in diameter as shown in the Fig. 1(a). In the image of elemental mapping, Fig. 1(b), the homogenous but scattered distribution of Si (green) and Cu (black) over the film indicates their homogeneous elemental distribution. In Raman spectrum, Fig. 1(c), the absence of the sharp peak at 516 cm^{-1}, which is characteristic of crystalline Si, but the presence of broad bands at 623, 478, 320 and 125 cm^{-1} reveals that the as-deposited Si-Cu film is amorphous .[13,14] Presence of the peaks of Cu substrate only in the XRD pattern (not shown) confirms this assignment.

3.2. Electrochemical behavior in diluted ionic liquid electrolyte

Electrochemical behavior of the Si-Cu electrodes were examined using constant current cycling at 35 μAcm^{-2}

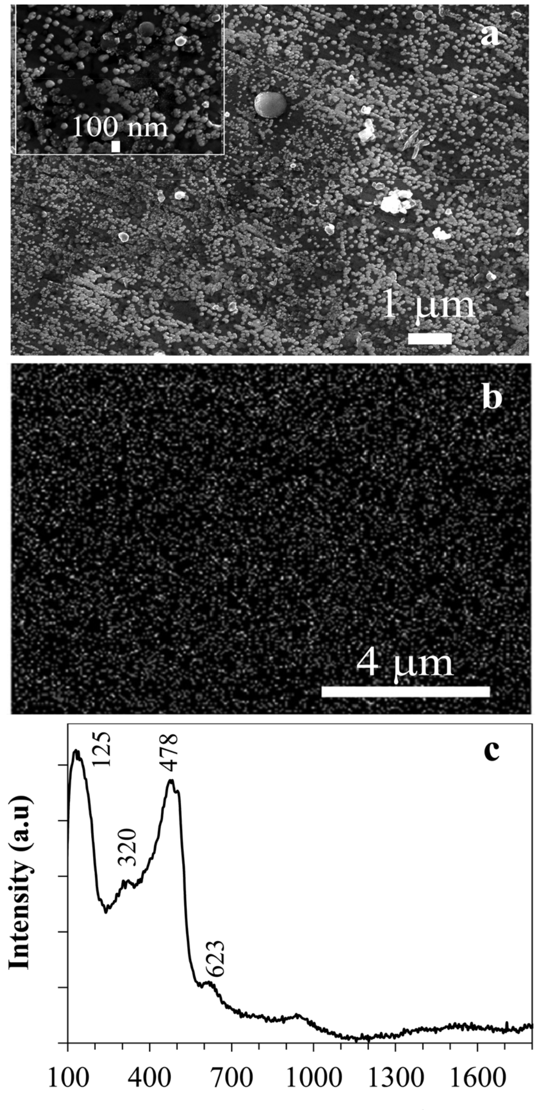

Fig. 1. Surface SEM image (a), elemental mapping of Si (green) and Cu (black) (b), and Raman spectrum (c) of the as-deposited Si-Cu electrode.

(~1C for $Li_{15}Si_4$) in the voltage region of 0.1-1.5 V.[15] Fig. 2(a-b) shows plots of discharge capacity *vs.* voltage for the Si-Cu film electrodes, which are obtained from the weight of whole electrode (Si + Cu). Differential capacity (dQ/dV) plots in Fig. 2(a'-b') shows better peak resolution of the Si reaction with lithium. In the electrolyte of 1 M $LiPF_6$/EC : DEC, the first cathodic process shows a broad peak ranged from 1.3 to 0.5 V, which is attributed to electrolyte reduction.[8,16] Significant cathodic peaks at 0.29-0.1 V are due to lithiation into the Si forming the Li_xSi.[15,17] On the reverse process, the anodic peaks near 0.55 V are due to delithiation from the Li_xSi, regenerating the Si. The first charge (lithiation) and discharge (delithiation) capacities are 2323 and 1223 $mAhg^{-1}$ (Fig. 2(a) and 3(a)) respectively, with the initial Coulombic efficiency of 53% (Fig. 3(b)). The low initial efficiency might be caused by reductive electrolyte decomposition together with irreversible lithiation and delithiation due to trapped lithium in the bulk of the Si particles. Cathodic and anodic peaks disappear and capacity fades rapidly near the 100th cycle, as observed in Fig. 2(b') and 3(a). This reflects that the surface layer formed during initial cycling is ineffective in protecting electrode surface but permits continuous interfacial reaction and changes in structural volume and particle morphology with repeated lithiation and delithiation. Efficiencies are changeable at 100-104% before the 100th cycle. Continuous formation of new surface species followed by their reformation process may provide additional discharge capacity to that of delithiation process.

On the contrary, in Fig. 2(b-b'), the Si-Cu electrode in 0.5 M LiTFSI/MPP-TFSI : DMC shows significantly improved capacity retention over 200 cycles and maintained peak resolution in the dQ/dV plot. The first charge process shows a similar feature to the electrode in 1 M $LiPF_6$/EC : DEC with a low capacity cathodic peak around 1.39 V, which is attributable to the reduction of DMC. The first charge and discharge capacities are 3091 and 1759 $mAhg^{-1}$ (Fig. 2(a) and 3(a)), respectively, corresponding to initial cycling efficiency of 57% (Fig. 3(b)). Still low initial efficiency indicates that in the diluted ionic liquid electrolyte the formation of the SEI layer by reductive electrolyte decomposition expenses extra charge capacity while passivating the electrode surface. In Fig. 2(b'), the shape of dominant peaks due to lithiation and delithiation near 0.25 and 0.5 V, respectively, is retained during 200 cycles. This verifies that electrode structure is preserved, and reversibility in lithiation and delithiation is somewhat increased, compared to those in the conventional electrolyte. The Si-Cu in the diluted ionic liquid electrolyte delivers high discharge capacity of > 1672 $mAhg^{-1}$ and discharge capacity retention of 88% over 200 cycles, as seen in Fig. 3(a). Efficiency in Fig. 3(b) increases to 95% till the 16th cycle, but suddenly decreases to ~83% and is recovered to 97% from the 48th cycle. Particle cracking might occur near the 16th cycle, at which the existing SEI layer can be damaged and fresh Li_xSi can be exposed to

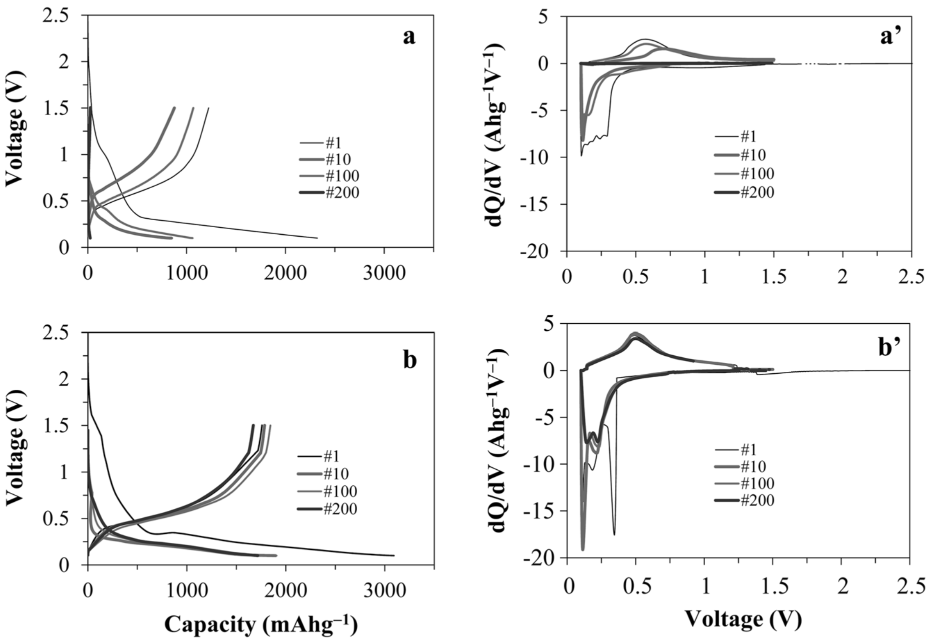

Fig. 2. Capacity *vs.* voltage plots of the lithium cells with the Si-Cu electrode cycled in (a) 1 M $LiPF_6$/EC : DEC and (b) 0.5 M LiTFSI/MPP-TFSI : DMC, and their differential capacity (dQ/dV) plots (a'-b').

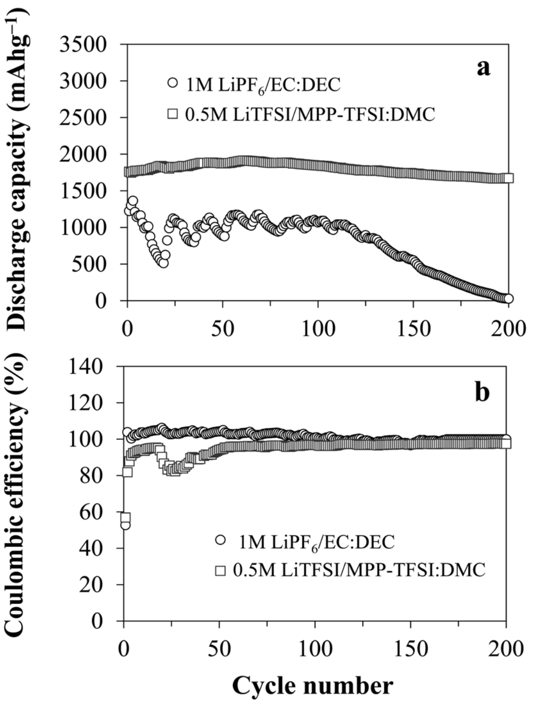

Fig. 3. Plots of discharge capacity (a) and Coulombic efficiency (b) of the lithium cells with the Si-Cu electrode cycled in 1 M $LiPF_6$/EC : DEC and 0.5 M LiTFSI/MPP-TFSI : DMC as a function of cycle number.

electrolyte. This leads to additional reductive electrolyte decomposition and lowering down of efficiencies. Newly produced electrode surface however appears to be effectively passivated with the SEI layer preventing from further interfacial reaction, resulting in efficiency retention of 97-98% till the 200th cycle.

3.3. Surface chemistry study using *ex-situ* IR spectroscopy

Fig. 4(a) shows the IR spectrum for the surface of the Si-Cu electrodes after cycling in the diluted ionic liquid electrolyte. Note that when the electrode was rinsed in DMC, soluble surface species could be washed off.

The spectrum shows strong absorbance peaks at 2956-2851 cm^{-1}, which is due to stretching of CH_3- methyl and -CH_2- methylene groups.[8,18] This is confirmed by their fingerprints at 1468 and 1447 cm^{-1}. Quite strong absorbance of alkyl group, in particular, -CH_2-methylene group, relative to other peaks indicates high concentration level of $CH_3(CH_2)_n$- polymer type SEI species. The source of alkyl group can be DMC and MPP cations. Another dominant peaks at 1580, 1558 and 1404 cm^{-1} are attributed to -C = O carbonyl groups of carboxylate metal salts $R\text{-}CO_2^{-}M^{n+}$ (R = alkyl group, M = Li/Si) with different bonding nature of carboxylate groups.[18] Peak positions of 1580 and 1558 cm^{-1} indicate that those carboxylate anion

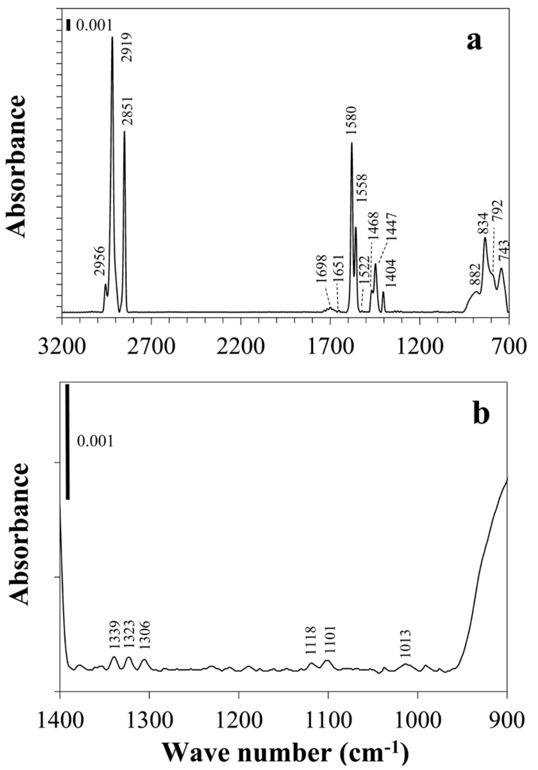

Fig. 4. IR spectrum of the Si-Cu electrode surface obtained after cycling in 0.5 M LiTFSI/MPP-TFSI : DMC (a), and its magnified spectrum in the region of 1400-900 cm^{-1} (b).

is bonded to metal cation as bidentate and bridge, respectively.[18)] Stronger absorbance of the peaks at 1580 cm^{-1} by bidentate-type carboxylate metal salts means its higher concentration level than bridge-type one. Considering significant absorbance peaks of alkyl group and the carboxylate metal salt functionalities, they are believed to belong to polymeric compounds, i.e., poly(carboxylate salt), together with organic carboxylate salt compounds. Relatively weak and broad peak centered at 1698 cm^{-1} is by -CO$_2$-R ester group.[8,18)] Tiny peaks at 1651 and 1306 cm^{-1} are characteristics of R-OCO$_2^-$M^{n+}, lithium alkyl carbonate metal salt.[19,20)] Trace of lithium carbonate, Li$_2$CO$_3$, is also observed at 1522 and 882 cm^{-1}. All of these species are typical decomposition products of carbonate-based solvents. In the magnified spectrum in the region of 1400-900 cm^{-1}, Fig. 4(b), tiny peaks at 1339 and 1323 are attributed to stretching modes of -SO$_2$- and 1118 and 1101 cm^{-1} to sulfate salts M$_2$(SO$_4^{2-}$)$_n$,[18)] which are the evidence of the TFSI decomposition.[8)]

Overall, spectral analysis results suggest that the SEI layer formed on Si-Cu cycled in the diluted electrolyte is mainly composed of poly(carboxylate metal salts). Recollecting that very thin SEI layer formed in the 1.0 M LiTFSI/MPP-TFSI,[8)] the polymeric SEI species is mostly originated from the decomposition of DMC, rather than MPP cations. This SEI layer appears to passivate the electrode surface better than that in the conventional electrolyte, resulting in greater capacity retention of 88% over 200 cycles. The data ensures that the control of electrolyte composition enables to regulate the SEI composition and stability, finally the cycling performance of Si-based anode materials.

4. Conclusions

We demonstrate the benefits of diluted ionic liquid electrolyte for the Si-Cu electrode in the aspects of viscosity and ionic conductivity as well as cycling performance and the SEI stability. The Si-Cu electrode cycled in the diluted ionic liquid electrolyte of 0.5 M LiTFSI/MPP-TFSI : DMC (1 : 1 volume ratio) shows significantly improved cycling stability with initial efficiency of 57% and capacity retention of 88% of maximum discharge capacity at the 200th cycle. By contrast, the electrode cycled in the conventional electrolyte results in rapid capacity fade. The electrode surface after cycling in the diluted ionic liquid electrolyte is covered dominantly by polymeric SEI species produced from the DMC decomposition, determined by IR spectroscopy. Effective passivation of electrode surface with polymeric surface species is believed to be the origin of improved cycling performance.

Acknowledgements

This work was supported by Mid-career Researcher Program through NRF grant funded by the MEST (No. 2010-0027665).

References

1. J.M. Tarascon and M. Armand, *Nature,* **414**, 359 (2001).
2. U. Kasavajjula, C. Wang and A.J. Appleby, *J. Power Sources,* **163**, 1003 (2007).
3. S.-J. Lee, J.-K. Lee, S.-H. Chung, H.-Y. Lee, S.-M. Lee and H.-K. Baik, *J. Power Sources,* **97-98**, 191 (2001).
4. S. Bourderau, T. Brousse and D.M. Schleich, *J. Power Sources,* **81-82**, 233 (1999).
5. J. Yin, M. Wada, K. Yamamoto, Y. Kitano, S. Tanase and T. Sakai, *J. Electrochem. Soc.,* **153**, A472 (2006).
6. H. Kim, B. Han, J. Choo and J. Cho, *Angew. Chem. Int. Ed.,* **47**, 10151 (2008).

7. C.C. Nguyen and S.-W. Song, *Electrochim. Acta,* **55**, 3026 (2010).
8. C.C. Nguyen and S.-W. Song, *Electrochem. Commun,* **12**, 1593 (2010).
9. M. Galiñski, A. Lewandowski and I. Stêpniak, *Electrochim. Acta,* **51** 5567 (2006).
10. A. Lewandowski and A. Swiderska-Mocek, *J. Power Sources,* **194**, 601 (2009).
11. *Principles and applications of lithium secondary batteries*, Hongreung Science, Edt. J.-K. Park, Seoul (2010).
12. A. Guerfi, M. Dontigny, P. Charest, M. Petitclerc, M. Lagacé, A. Vijh and K. Zaghib, *J. Power Sources,* **195**, 845 (2010).
13. D. Han, J.D. Lorentzen, J. Weinberg-Wolf and L.E. McNeil, *J. Appl. Phys.,* **94**, 2930 (2003).
14. V. Baranchugov, E. Markevich, E. Pollak, G. Salitra and D. Aurbach, *Electrochem. Commun.,* **9**, 796 (2007).
15. M.N. Obrovac and L. Christensen, *Electrochem. Solid-State Lett.,* **7**, A93 (2004).
16. K. Xu, *Chem. Rev.,* **104**, 4303 (2004).
17. E. Pollak, G. Salitra, V. Baranchugov and D. Aurbach, *J. Phys. Chem. C,* **111**, 11437 (2007).
18. G. Socrates, *Infrared Characteristic Group Frequencies, Tables and Charts, 2nd ed*, John Wiley & Sons, New York (1994).
19. G.V. Zhuang, H. Yang, J. Philip N. Ross, K. Xu and T.R. Jow, *Electrochem. Solid-State Lett.,* **9**, A64 (2006).
20. D. Aurbach, M.L. Daroux, P.W. Faguy and E. Yeager, *J. Electrochem. Soc.,* **134**, 1611 (1987).