Short communication

Application of bis(fluorosulfonyl)imide-based ionic liquid electrolyte to silicon–nickel–carbon composite anode for lithium-ion batteries

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ABSTRACT

An ionic liquid electrolyte containing bis(fluorosulfonyl)imide (FSI) anion without any solvent is applied to a silicon–nickel–carbon (Si–Ni–carbon) composite anode for rechargeable lithium (Li)-ion batteries. The FSI-based ionic liquid electrolyte successfully provides a stable, reversible capacity for the Si–Ni–carbon anode, which is comparable to the performance observed in a typical commercialized solvent-based electrolyte, while a common ionic liquid electrolyte containing bis(trifluoromethanesulfonyl)imide (TFSI) anion without FSI presents no reversible capacity to the anode at all. Ac impedance analysis reveals that the FSI-based electrolyte provides very low interfacial and charge-transfer resistances at the Si-based composite anode, even when compared to the corresponding resistances observed in a typical solvent-based electrolyte. Galvanostatic cycling of the Si-based composite anode in the FSI-based electrolyte with a charge limitation of 800 mAh g^{-1} is stable and provides a discharge capacity of 790 mAh g^{-1} at the 50th cycle, corresponding to a cycle efficiency of 98.8%.

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1. Introduction

Lithium (Li)-ion batteries have been utilized as power supplies of electronic devices such as cell phones and laptop computers. Rechargeable Li batteries, typically Li-ion batteries, are expected to make further improvements in energy density and cycle life in the future, because improved rechargeable Li batteries will certainly contribute to the actualization of a plug-in hybrid electric vehicle (P-EV) as well as a "pure" electric vehicle (EV). However, ethylene carbonate (EC)-based solvent systems used as a conventional electrolyte in Li-ion batteries pose a fire risk in the event of overcharge, crush, or short circuit. To resolve this crucial problem, ionic liquids have attracted increasing attention in the development of advanced rechargeable Li batteries due to their diverse favorable properties such as a wide electrochemical potential window, acceptable ionic conductivity at ambient temperature, high thermal stability, and negligible vapor pressure implying incombustibility [1–17].

Recently, our group [9–11], Passerini and co-workers [12,13], Zaghib and co-workers [14], Seki et al. [15], and Matsumoto et al. [16,17] have reported on ionic liquid electrolytes based

on bis(fluorosulfonyl)imide (FSI) for rechargeable Li batteries. In particular, FSI-based electrolytes containing Li-ion exhibited practical ionic conductivity, and a natural graphite/Li cell with FSI-based electrolytes containing Li bis(trifluoromethanesulfonyl)imide (LiTFSI) showed excellent cycle performance without any solvent [9,10].

Graphite has been commonly used as a commercial anode material in Li-ion batteries because of its stable charge–discharge performance, although its capacity is limited to 372 mAh g^{-1}. To overcome the capacity limitation of graphite, Li-alloy anodes with a high specific capacity have attracted much attention [18–20]. In particular, the class of Silicon (Si) anode materials has been reported as the most promising anode alternative to commercial graphite anodes thanks to a much higher theoretical capacity (4200 mAh g^{-1}) of their Li-alloy, Li$_{4.4}$Si [21,22]. However, their large specific volume change occurs during Li insertion/extraction reactions at Si-based anode materials, and this causes rapid capacity fading with charge/discharge cycles by the pulverization of mainly Si [23,24]. Consequently, various approaches to improving their cycle life have been proposed to prevent mechanical electrode degradation. Si–carbon composites were previously reported as an effective avenue to improve the cycle life of Si-based anode materials because carbon acts as a mechanical and electrochemical buffer [23,25]. On the other hand, Si and nickel (Ni) composite

anode materials, where Ni was dispersed uniformly in a Si matrix, exhibited improved cyclic performance because Ni increases the electric conductivity of composites [26,27]. Furthermore, Lee et al. reported on electrochemical characteristics of Si–Ni–carbon and (Si–Ni alloy)–carbon composites in an attempt to combine the respective favorable properties of Ni and carbon [28,29].

Their large reversible capacity (approximately 800 mAh g^{-1}) and good cycleability may prove that such an Si–Ni–carbon composite is an alternative to conventional graphite-based anode materials for Li-ion batteries, which typically contain an organic solvents-based electrolyte. Nonetheless, to the best of our knowledge, there has been no report on the application of ionic liquid electrolytes without any solvent, that is, "pure" ionic liquids, to a Si–Ni–carbon composite anode; most ionic liquids without an appropriate solvent are easily decomposed with various anodes, including carbon anodes as well as Si-based anodes, for Li-ion batteries when they are charged.

In this study, we focus on an FSI-based ionic liquid as a promising electrolyte compatible with a Si–Ni–carbon composite anode. This approach appears promising because we already found that an FSI-based electrolyte provides excellent reversibility with a graphite anode without any solvent [9–11]. Here, we compare the charge–discharge performance of the above composite anode in an ionic liquid electrolyte with the corresponding performance of the anode in a conventional solvent-based electrolyte. This study suggests that the proposed FSI-based electrolyte without any solvent is compatible with the Si–Ni–carbon composite anode.

2. Experimental

The ternary Si–Ni–carbon composite was synthesized by a two-step mechanical milling process. First, the binary Si–Ni composite was synthesized by the following procedure: Si (325 mesh, Rare Metallic Co. Ltd.) and Ni (200 mesh, Rare Metallic Co. Ltd.) powders in a weight ratio of 6:1 were introduced into a stainless steel vessel with steel balls at a ball-to-powder weight ratio of 15:1. The vessel was filled with argon to prevent oxidation of the starting materials. The mixture was milled at 400 rpm for 4 h. Next, natural graphite (HQB12, Hydro Québec) as carbon source was added to the resulting Si–Ni composite at a graphite-to-composite weight ratio of 1:1. The Si–Ni–carbon composite was obtained by the second ball-milling at 400 rpm for 30 min. The crystalline phase of the final powder was observed by XRD with Cu Kα radiation.

For electrochemical measurements, the Si–Ni–carbon composite electrode was fabricated as follows: the obtained Si–Ni–carbon composite powder was mixed with acetylene black and polyvinylidene fluoride (PVdF) in a weight ratio of 75:15:10 in a solvent, N-methylpyrrolidinone (NMP). The obtained slurry was coated onto a Cu foil and dried at 85 °C for 24 h under a vacuum. The foil electrode was cut into a disk of 1.13 cm^2 in area, with a total thickness of 43 μm including the copper foil thickness of 18 μm.

Two kinds of ionic liquid, 1-ethyl-3-methylimidazolium (EMIm)-FSI and EMIm-TFSI, were produced by Dai-ichi Kogyo Seiyaku Co., Ltd. These ionic liquids contain less than 10 ppm (w/w) of moisture and 2 ppm (w/w) of halide and alkali metal-ion impurities. Battery-grade LiTFSI was purchased from Kishida Chemical Co., Ltd. and used without further purification. 1.0 mol dm^{-3} (hereafter, M) LiPF$_6$ in a 1:1 (v/v) mixture of ethylene carbonate (EC) with dimethyl carbonate (DMC), that is, 1.0 M LiPF$_6$ EC + DMC was used as a reference solvent-based electrolyte in comparison with the characteristics of ionic liquid electrolytes. Li-ion-containing ionic liquid electrolytes were prepared by dissolving LiTFSI in EMIm-TFSI or EMIm-FSI so that the LiTFSI concentration was 0.3 mol kg^{-1}: these are denoted by LiTFSI/EMIm-TFSI and LiTFSI/EMIm-FSI, respectively.
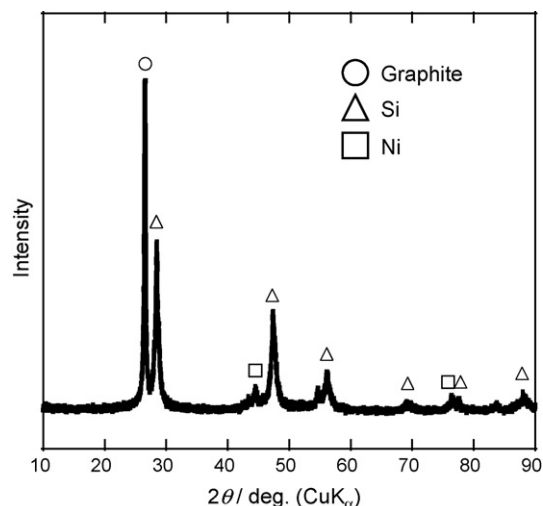

Fig. 1. X-ray diffraction pattern of Si–Ni–carbon composite prepared by high-energy mechanical milling at a weight ratio of Si:Ni:C = 6:1:7.

A two-electrode coin-type cell was used as a charge–discharge test cell. A battery-grade Li foil (Honjo Metal Co., Ltd.) was used as a counter electrode, and a separator film (075E02, Nippon Sheet Glass Co., Ltd.) was soaked in ionic electrolyte solutions under vacuum before cell assembly. The performance of the Si–Ni–carbon composite electrode was measured in a range between 0.005 and 1.5 V (vs. Li counter electrode) at 25 °C, using a BTS2004W battery tester (Nagano Co., Ltd.). Ac impedance of the Si–Ni–carbon composite electrode at open-circuit voltages was measured with an impedance analyzer (S1 1280B, Solartron) after a duration of 30 min following the first charging to 0.005 V at a rate of 500 mA g^{-1} using a two-electrode cell with an Li sheet as a counter electrode. The scanned frequencies were from 20 kHz to 0.01 Hz, and the ac amplitude was 10 mV$_{p-p}$ at 25 °C.

3. Results and discussion

The XRD pattern of the obtained Si–Ni–carbon composite material is shown in Fig. 1. Simple Si and Ni peaks are observed in the composite without a Si–Ni alloy or NiSi$_x$ peak. There exist only the crystalline diffraction peaks of Si, Ni and natural graphite, while no other impurity phases are detected.
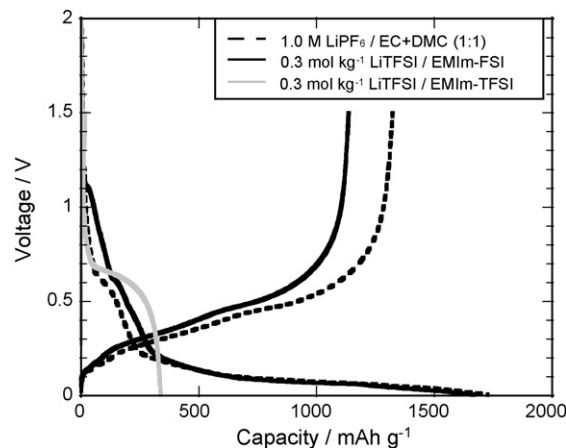

Fig. 2. Charge–discharge profiles of Si–Ni–carbon composite electrode at the first cycle with 0.3 mol kg^{-1} LiTFSI/EMIm-FSI, 0.3 mol kg^{-1} LiTFSI/EMIm-TFSI, and 1.0 M LiPF$_6$/EC + DMC at charge–discharge current of 500 mA g^{-1}.
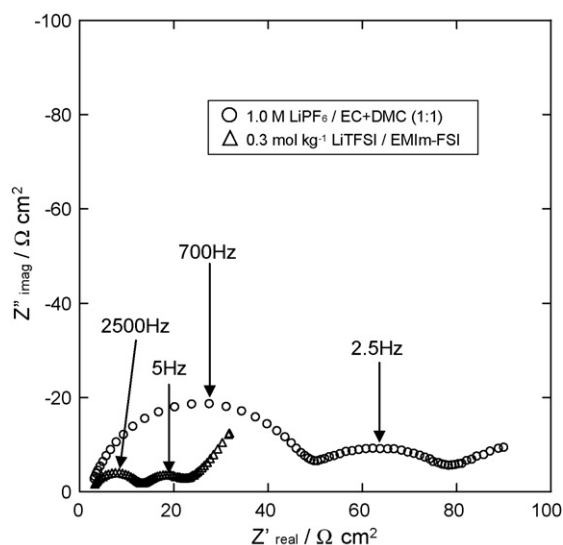
Fig. 3. Nyquist plots of ac impedance for Si–Ni–carbon composite electrode at the first charge to 0.005 V with 0.3 mol kg^{-1} LiTFSI/EMIm-FSI and 1.0 M LiPF$_6$/EC + DMC. Charge current: 500 mA g^{-1}.

Fig. 2 shows the charge–discharge profiles of the Si–Ni–carbon composite anode with various electrolytes in the first cycle. The LiTFSI/EMIm-TFSI system induces a significant irreversible reduction of the EMIm cation at ca. 0.7 V at the first charge and provides negligible capacity at the subsequent first discharge. Consequently, in the LiTFSI/EMIm-TFSI system, no reversible Li insertion/extraction occurs at the composite electrode, suggesting that irreversible reduction of the EMIm cation would form a blocking layer at the composite anode, similar to a graphite anode [9,10]. In contrast, the LiTFSI/EMIm-FSI system provides typical charge and discharge plateaus corresponding to Li intercalation and de-intercalation, respectively; the first discharge capacity is 1136 mAh g^{-1} (this weight includes Si, Ni, and carbon, and hereafter too). Although this value is somewhat lower than the value obtained in the LiPF$_6$/EC + DMC system, 1323 mAh g^{-1}, this result clearly indicates that the present FSI-based ionic liquid electrolyte provides practical reversibility for an Si-based composite anode, which has never been observed in non-FSI ionic liquid electrolytes without any additive. The presence of FSI can promote Li cation migration into an anode and, at the same moment, can prevent EMIm decomposition at ca. 0.6 V. This effect implies that FSI anion can mobilize Li cation escaping from an electrostatic inter-ionic cage of ionic components, and in consequence, EMIm cation alternatively recedes from the electrode interface, hence avoiding its reductive decomposition, although such possibility has not fully been confirmable in our previous article [11].

As an analysis for the interfacial behavior of the composite anode, ac impedance spectroscopy is applied to the present electrode/electrolyte systems. Fig. 3 shows Nyquist plots after charging the Si–Ni–carbon composite electrode to 0.005 V at 500 mA g^{-1} in the LiPF$_6$/EC + DMC and LiTFSI/EMIm-FSI systems. The LiTFSI/EMIm-TFSI system is excluded from this analysis because charging in the system is essentially impossible, and so we cannot compare its impedance response with the others at the same charging status. The combination of a semicircle in the high frequencies and a smaller, flattened semicircle together with a short slope in the low frequencies is observed in LiPF$_6$/EC + DMC. The semicircle in the high frequencies can be attributed to the impedance of a surface chemical layer, while the low-frequency semicircle would be related to a charge–transfer resistance as a main reaction process of the electrode [10,30]. On the other hand, the combination of a very small semicircle in the higher frequen-

cies, compared to that in the above LiPF$_6$/EC + DMC system, and another tiny semicircle together with a clear slope in the low frequencies is observed in the LiTFSI/EMIm-FSI system. These results suggest that not only the resistance of a chemical interface derived from the LiTFSI/EMIm-FSI system but also the reaction resistance for the Li insertion/extraction into/from the Si–Ni–carbon composite electrode in this ionic liquid is extremely low when compared to the respective resistances generated in a conventional solvent-based electrolyte. Such a marked contrast between the FSI-based ionic liquid system and the conventional electrolyte system was also observed with a graphite anode [10].

Fig. 4 shows the cycle dependency of discharge capacity of the Si–Ni–carbon composite electrode in the tested electrolytes at 500 mA g^{-1}. No discharge capacity is observed at all for the LiTFSI/EMIm-TFSI system in the present galvanostatic cycling, which follows the irreversible first cycle shown in Fig. 2. In contrast, the discharge capacity of the Si–Ni–carbon composite electrode in the LiTFSI/EMIm-FSI is 932.5 mAh g^{-1} even at the 20th cycle. The charge–discharge cycle efficiency at each cycle is ca. 98%. Observed capacity fading with cycling would be mainly due to the gradual loss of electrical contact inside the electrode, which is induced by a substantial volume change of Si with Li insertion/extraction rather than ionic liquid electrolyte decomposition. In fact, although the conventional EC + DMC system shows the highest capacitance, it still involves a capacity fading. Because the viscosity of LiTFSI/EMIm-FSI
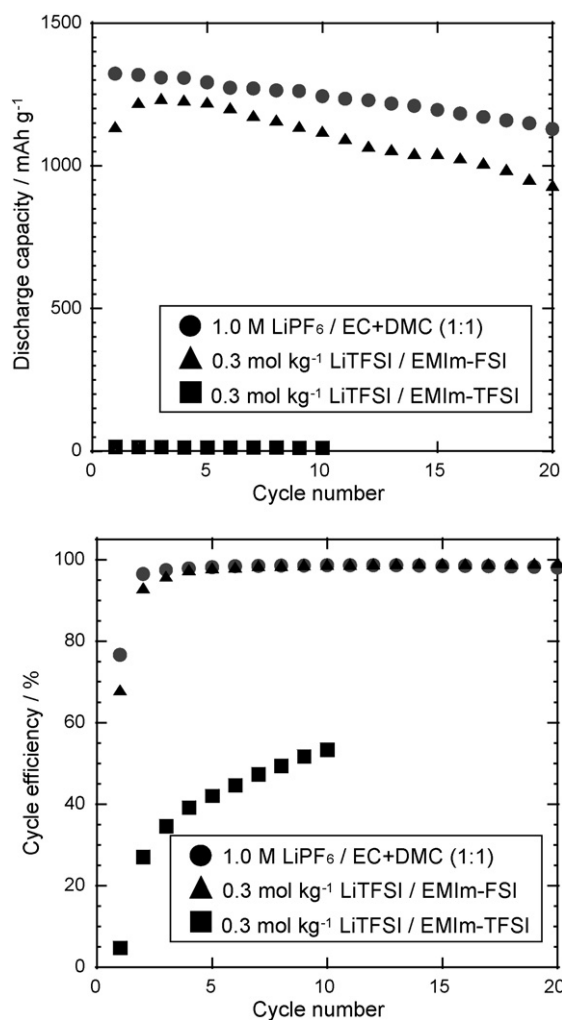

Fig. 4. Cyclic performance of Si–Ni–carbon composite electrode with 0.3 mol kg^{-1} LiTFSI/EMIm-FSI, 0.3 mol kg^{-1} LiTFSI/EMIm-TFSI, and 1.0 M LiPF$_6$/EC + DMC at charge–discharge current of 500 mA g^{-1}.

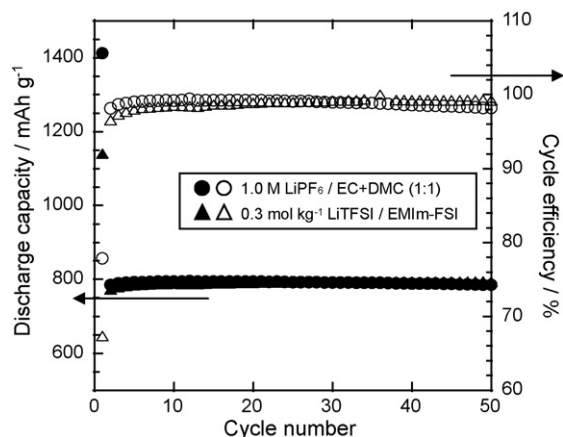**Fig. 5.** Cyclic performance of Si–Ni–carbon composite electrode with 0.3 mol kg^{-1} LiTFSI/EMIm-FSI and 1.0 M LiPF$_6$/EC + DMC at charge–discharge current of 800 mA g^{-1}, with charge limitation of 800 mAh g^{-1} except for the 1st charge.

is much (ca. 10-fold) higher than that of LiPF$_6$/EC + DMC [10], the present high-rate (500 mA g^{-1}) galvanostatic charging–discharging causes a capacity loss in LiTFSI/EMIm-FSI when compared to that in LiPF$_6$/EC + DMC. This means that, although the interfacial resistance obtained at the small ac amplitude of 10 mV$_{p-p}$ is very low in LiTFSI/EMIm-FSI (Fig. 3) its high-rate galvanostatic capability is inevitably limited by its high viscosity.

To restrain the capacity fading, we limited the charge capacity to 800 mAh g^{-1} after the first cycle because this limitation could relieve the volume change of the Si–Ni–carbon composite with Li insertion/extraction. As shown in Fig. 5, the Si–Ni–carbon composite electrode in the LiTFSI/EMIm-FSI system exhibits significantly stable, reversible discharge capacity over 50 cycles with this limitation; the reversible capacity at the 50th cycle is 790 mAh g^{-1}, which corresponds to a coulombic cycle efficiency of 98.8% (=790/800). These values and the observed stability are almost equivalent to those in the LiPF$_6$/EC + DMC system. Another notable point is that a relatively high current is applicable to the FSI-based ionic liquid electrolyte/Si-based anode: 800 mA g^{-1} (corresponding to 1 C rate in Fig. 5), since an FSI-based electrolyte has an exceptionally low viscosity among ionic liquids [9].

As observed above, we found that an ionic liquid electrolyte containing FSI anion provides reversible, stable charge–discharge behavior to a Si-based composite anode without any solvent additives. This is a rare successful case in various attempts to apply ionic liquid electrolytes to Si-based anodes. Moreover, note that a very high current, e.g., 800 mA g^{-1}, is applicable to the proposed composite electrode in the FSI-based electrolyte; 800 mA g^{-1} corresponds to 1 C rate in Fig. 5. As we already reported, the LiTFSI/EMIm-FSI electrolyte also provides an excellent reversibility to a graphitized anode [9–11]; therefore, ionic liquids containing FSI are promising electrolytes when we attempt to construct safe, stable Li-ion batteries with practical charge–discharge performance.

4. Conclusions

The present ionic liquid electrolyte based on FSI successfully provides a stable, reversible capacity for a Si–Ni–carbon composite anode without any solvent, while a common TFSI-based ionic liquid electrolyte without FSI offers no reversible capacity for the anode at all. In particular, galvanostatic cycling of the Si-based composite anode in the FSI-based electrolyte with a charge limitation of

800 mAh g^{-1} provides a discharge capacity of 790 mAh g^{-1} even at the 50th cycle. Based on ac impedance analysis, such excellent performance with FSI would correlate with very low interfacial and charge–transfer resistances at the Si-based composite anode. The proposed Si–Ni–carbon composite electrode is expected to improve the energy density of Li-ion batteries because the capacity of the electrode is 2.1 times as high as the theoretical capacity of a graphite anode, even with the above capacity limitation. Therefore, the combination of the FSI-based ionic liquid electrolyte and the Si-based anode may achieve a safe Li-ion battery with an excellent energy density.

References

[1] T. Sato, T. Maruo, S. Marukane, K. Takagi, J. Power Sources 138 (2004) 253.
[2] M. Holzapfel, C. Jost, P. Novak, Chem. Commun. 10 (2004) 2098.
[3] M. Holzapfel, C. Jost, A. Prodi-Schwab, F. Krumeich, A. Wursig, H. Bupa, Carbon 43 (2005) 1488.
[4] K. Ui, T. Minami, K. Ishikawa, Y. Idemoto, N. Koura, J. Power Sources 146 (2005) 698.
[5] H. Zheng, K. Jiang, T. Abe, Z. Ogumi, Carbon 44 (2006) 203.
[6] H. Nakagawa, Y. Fujino, S. Kozono, Y. Katayama, T. Nukuda, H. Sakaebe, H. Matsumoto, K. Tatsumi, J. Power Sources 174 (2007) 1021.
[7] T. Sato, S. Marukane, T. Narutomi, T. Akao, J. Power Sources 164 (2007) 390.
[8] J. Saint, A.S. Best, A.F. Hollenkamp, J. Kerr, J.-H. Shin, M.M. Doeff, J. Electrochem. Soc. 154 (2008) A172.
[9] M. Ishikawa, T. Sugimoto, M. Kikuta, E. Ishiko, M. Kono, J. Power Sources 162 (2006) 658.
[10] T. Sugimoto, M. Kikuta, E. Ishiko, M. Kono, M. Ishikawa, J. Power Sources 183 (2008) 436.
[11] T. Sugimoto, Y. Atsumi, M. Kikuta, E. Ishiko, M. Kono, M. Ishikawa, J. Power Sources 189 (2009) 802.
[12] G.B. Appetecchi, M. Montanino, A. Balducci, S.F. Lux, M. Winter, S. Passerini, J. Power Sources 192 (2009) 599.
[13] S.F. Lux, M. Schmuck, G.B. Appetecchi, S. Passerini, M. Winter, A. Balducci, J. Power Sources 192 (2009) 606.
[14] A. Guerfi, S. Duchesne, Y. Kobayashi, A. Vijh, K. Zaghib, J. Power Sources 175 (2008) 866.
[15] S. Seki, Y. Kobayashi, H. Miyashiro, Y. Ohno, Y. Mita, N. Terada, J. Phys. Chem. C 112 (2008) 16708.
[16] H. Matsumoto, H. Sakaebe, K. Tatsumi, M. Kikuta, E. Ishiko, M. Kono, J. Power Sources 160 (2006) 1308.
[17] H. Sakaebe, H. Matsumoto, K. Tatsumi, Electrochim. Acta 53 (2007) 1048.
[18] R. Yazami, K. Zaghib, M. Deschamps, J. Power Sources 52 (1994) 55.
[19] J.O. Besenhard, J. Yang, M. Winter, J. Power Sources 68 (1997) 87.
[20] J. Yang, Y. Takeda, N. Imanish, O. Yamamoto, J. Electrochem. Soc. 146 (1999) 4009.
[21] J. Yang, M. Winter, J.O. Besenhard, Solid State Ionics 90 (1996) 281.
[22] Y. Liu, K. Hanai, J. Yang, N. Imanishi, A. Hirano, Y. Takeda, Solid State Ionics 168 (2004) 61.
[23] I.A. Courtney, J.R. Dahn, J. Electrochem. Soc. 144 (1997) 2045.
[24] H. Li, X. Huang, L. Chen, Z. Wu, Y. Liang, Electrochem. Solid State Lett. 2 (1999) 547.
[25] Z.P. Guo, Z.W. Zhao, H.K. Liu, S.X. Dou, J. Power Sources 146 (2005) 190.
[26] N. Dimov, S. Kugino, M. Yoshio, Electrochim. Acta 48 (2003) 1579.
[27] I.-S. Kim, P.N. Kumta, Electrochem. Solid State Lett. 7 (2004) A44.
[28] M.-S. Park, S. Rajendran, Y.-M. Kang, K.-S. Hana, Y.-S. Hand, J.-Y. Lee, J. Power Sources 158 (2006) 650.
[29] M.-S. Park, Y.-J. Lee, S. Rajendran, M.-S. Song, H.-S. Kim, J.-Y. Lee, Electrochim. Acta 50 (2005) 5561.
[30] D. Aurbach, K. Gamolsky, B. Markovsky, Y. Gofer, M. Schmidt, U. Heider, Electrochim. Acta 47 (2002) 1423.