

Electrochemical behaviors of silicon based anode material

Masaki Yoshio*, Takaaki Tsumura, Nikolay Dimov

Department of Applied Chemistry, Saga University, 1 Honjo, Saga 840-8502, Japan

Available online 1 June 2005

Abstract

Mixed silicon/graphite anode materials have been prepared by means of simple mechanical milling process. Research reveals that the microstructural changes, accompanying the electrochemical alloying/de-alloying operations lead to a macrostructural deformations of the anodes. The key step for improving of such composites, therefore, could be sought in alternative electrode configurations or textures, preserving the electrodes from the detrimental effect of silicon hosts volume variations.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Silicon/graphite composites; Lithium-ion batteries; Negative electrode materials; Electrode deformation

1. Introduction

Due to the worldwide research efforts, the capacity of the practical carbonaceous anodes has recently almost reached the theoretical value of the composition LiC_6 . Further improvement of the lithium-ion batteries is, therefore, closely related to the adoption of new anode materials, having higher specific capacity. There are many candidate binary alloys and intermetallic compounds with high theoretical capacity, specially the metals from the third and fourth column of the periodic table. Silicon is the most attractive one because of its low atomic weight, high lithium uptake (in theory up to $\text{Li}_{22}\text{Si}_5$) and low alloying potential versus Li. Despite of these favorable features, the commercialization of Si-based anodes has been hindered because the practical preparation of Li-alloying metal contained anodes is not an easy task. The difficulty arises by the fact that alloying typically leads to direct destruction of the initial crystal lattice, followed by a huge volumetric expansion of the parent solid phase, which results in an extremely bad cyclic performance. There are two generally known approaches to overcome the detrimental effect of the silicon solid phase volume variations:

- (i) Thin silicon films directly deposited on the current collector. Advantage of this approach is the lack of binder

and any other parasite mass in the electrode. The drawback is that the processes used for preparation of such films (rf-magnetron sputtering or vacuum deposition) are not suitable for scaling-up. Moreover, the electrochemical performance is much worse when the film is thicker than ca. $1\ \mu\text{m}$ due to the increase in diffusion length of Li, the increase of resistance and mechanical stress induced during the charging/discharging operations [1–3].

- (ii) Silicon-containing composite materials, where elemental silicon or binary silicon compound is used as a starting material. Attempts to prepare such electrodes have focused on reducing the particle size of the host material, using multi-phase materials or intermetallic compounds [4–8]. The main advantage of the composite approach is that electrodes are prepared by means of well-known and widely adopted electrode fabrication techniques. The major problem, however, is that the preparation and optimization of these formulations is not a trivial task. Although the composites do not offer specific capacities as high as those of the pure silicon films, they might be a viable alternative to the pure carbonaceous anodes.

The advantage of using higher capacity anode material can be easily quantified. Consider a given cathode material with capacity C_C , it may vary from ca. $140\ \text{mAh g}^{-1}$ (LiCoO_2 , spinels) to ca. $200\ \text{mAh g}^{-1}$ (LiMnO_2 and its derivatives). There is a simple relationship between the total capacity of the electrode material (cathode + anode) as a function of the

* Corresponding author. Tel.: +81 952 28 8673; fax: +81 952 28 8591.
E-mail address: yoshio@ccs.ce.saga-u.ac.jp (M. Yoshio).

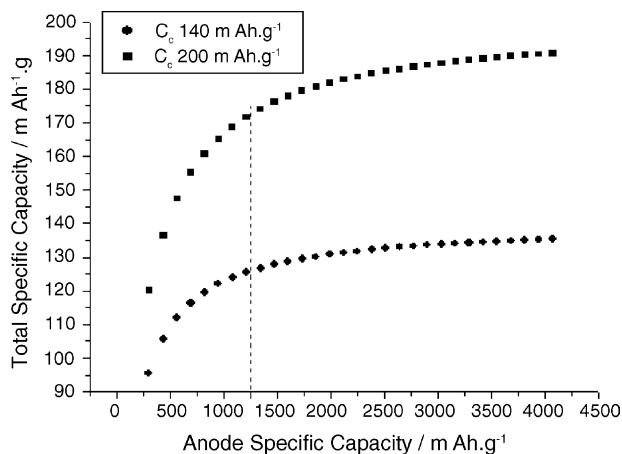


Fig. 1. Total capacity of the LIB material, presented as a function of the anode capacity (C_A). Cathodes with capacities 140 and 200 mAh g^{-1} are considered. Two regions can be distinguished—comparatively fast increase for C_A variation 300–1200 mAh g^{-1} , and a plateau-like when anode capacity exceeds ca. 1200 mAh g^{-1} .

anode specific capacity C_A . A qualitative expression for the total capacity with the variation of the anode specific capacity is:

$$\text{Total} = \frac{C_C}{1 + \frac{C_C}{C_A}} = \frac{C_A C_C}{C_A + C_C} \quad (\text{mAh g}^{-1}) \quad (1)$$

From equation (1), we recognize that for a fixed specific cathode capacity C_C , the total specific capacity does not increase linearly with the linear increase of C_A . The function presented with Eq. (1) is plotted in Fig. 1. This function increases quickly at the initial with the increase of C_A and then saturation takes place. This behavior can be further confirmed by the limit $C_A \rightarrow \infty$. It can be clearly seen that in the latter case the derivative

$$\frac{d(\text{Total})}{d(C_A)} = \frac{(C_C)^2}{(C_C + C_A)^2} \rightarrow 0 \quad \text{as } C_A \rightarrow \infty \quad (2)$$

The rate at which the total capacity increase will depend on the value of C_C . As seen in the figure, there are two regions—comparatively fast increase in the total capacity for C_A variation 300–1200 mAh g^{-1} , and the region with a smaller slope when the anode capacity exceeds ca. 1200 mAh g^{-1} . Therefore, the most noticeable improvement of the LIB can be done if the presently used carbonaceous anode can be replaced with one having capacity of the order of 1000 mAh g^{-1} —a value which could be in principle reached by means of composite silicon-based anodes. Due to the voltage reduction the energy density in this case would be slightly higher compared with the case of pure graphite anode. However, the combination of high voltage cathodes and composite silicon anodes can boost up the energy density of LIB to levels comparable with those of the present-day primary lithium cells.

2. Experimental

Screening experiments revealed that the best results are obtained when the amount of silicon in the Si/C composite does not exceed 30 wt%. Silicon powder with an average particle grain size of 1 μm was used as received from Mitsui Kozan Co. It was mixed with natural graphite (NG-7, Japan; weight ratio, 3:7) and 10 wt% of silver powder (Fraunhofer Institut, Germany), which was added with respect to the weight of the Si/C mixture. The mixture was then milled for 5 h under Ar at 250 rpm by means of a rotary ball mill (Fritsch, Germany). The electrode preparation technique is the common method used by LIB industries. The dry Si/C composite was mixed with an appropriate amount of 9 wt% polyvinylidene fluoride (PVDF) in *N*-methylpyrrolidone (NMP) solution. It was then agitated and the resulted slurry was pasted on a copper foil or nickel foam current collector, respectively, and dried at 120 $^{\circ}\text{C}$. All electrode preparation steps were performed under an Ar atmosphere to minimize oxidation of the silicon powder. Circle-shaped electrodes were punched from the copper foil, then pressed and cycled in a coin cell versus Li metal. The nickel foam electrodes were first cut from the nickel foam sheet. The slurry used for copper foil electrodes preparation was diluted with NMP (slurry:NMP weight ratio \sim 3:1), pasted on the nickel foam and dried under the same conditions as the copper foil electrodes.

3. Results and discussion

Our previous study showed that graphite phase plays an important role for improving the cycling performance of the mixed Si/C composite, serving as a media that prevents active particle–particle interactions [9–11]. As shown previously [12], decreasing of silicon particle size in the mixed Si/C composite allowed preparation of morphologically sta-

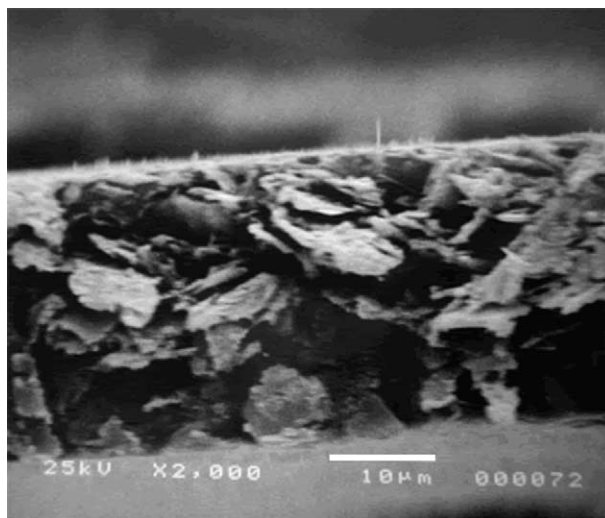


Fig. 2. Structure of the Si:C composite electrode prepared using copper foil current collector.



Fig. 3. Back side view of the Si:C composite electrodes. Active material pasted on a copper foil. Left image: before cycling; right image: after cycling.

ble anodes with improved cycling performance. However, compared with pure graphite anodes, the cycling life of electrodes prepared using a copper foil current collector remained unsatisfactory. As shown in Figs. 2 and 3, those electrodes became deformed after prolonged cycling. Such behavior was never observed with the pure carbonaceous anodes prepared and tested in similar conditions. Therefore, the microstructural changes of the silicon-containing composite anodes led

to macrostructural deformations of the electrode. To check the importance of this factor, an alternative nickel foam current collector and the electrode prepared with it is shown in Fig. 4. A comparative cycling test for both configurations is shown in Figs. 5 and 6. As seen from the figures, the cycling performance of nickel foam electrodes is greatly improved on the expense of a low coulombic efficiency over the ini-

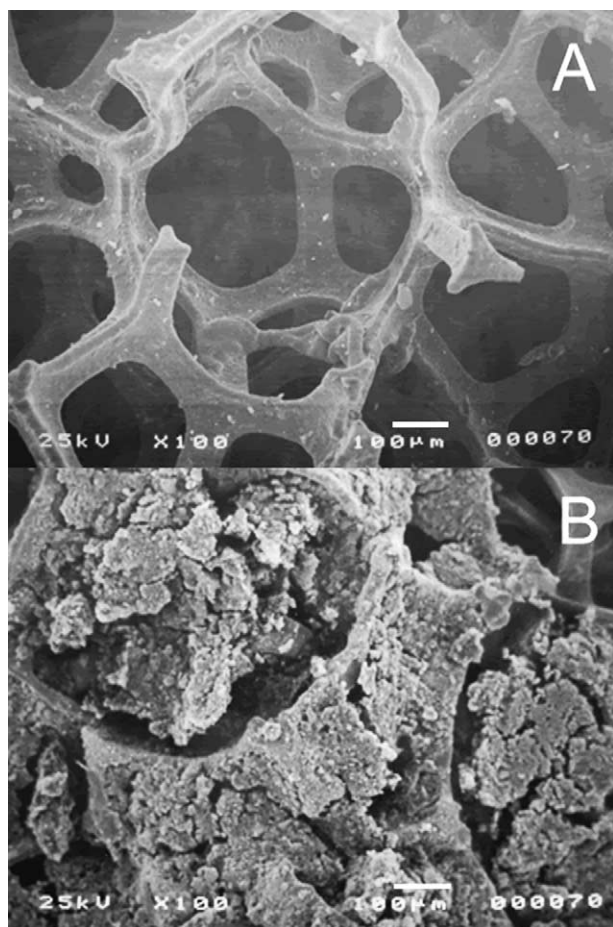


Fig. 4. (A) The structure of the 3D nickel foam current collector. (B) The electrode prepared using the nickel foam current collector.

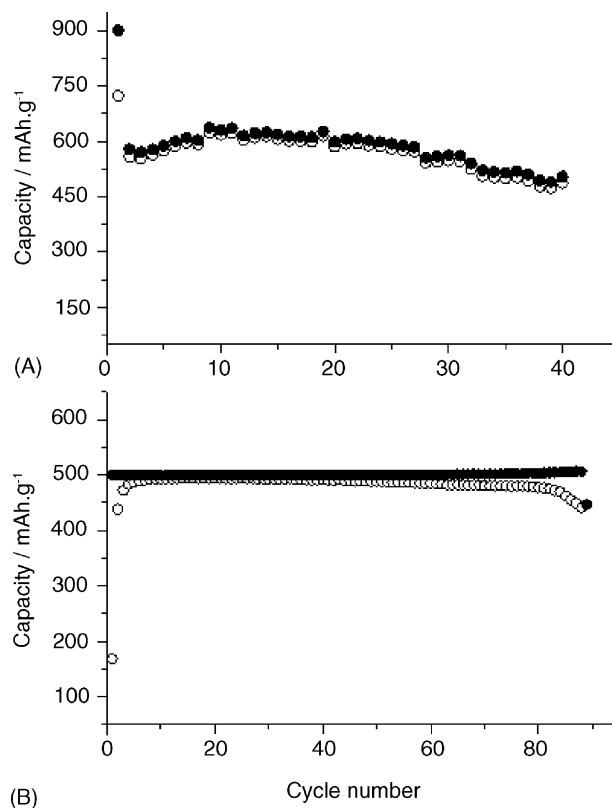


Fig. 5. Cycling test of Si:C (3:7) with addition of 10 wt% Ag composite anode, pasted on a copper foil current collector. (A) Galvanostatic cycling at current density 1.0 mA cm^{-2} ($\approx 0.35 \text{ mA mg}^{-1}$) between 40 mV and 1.5 V. (B) Potentiostatic constant capacity (500 mAh g^{-1}) cycling at a current density 1.0 mA cm^{-2} ($\approx 0.35 \text{ mA mg}^{-1}$) between 5 mV and 1.5 V.

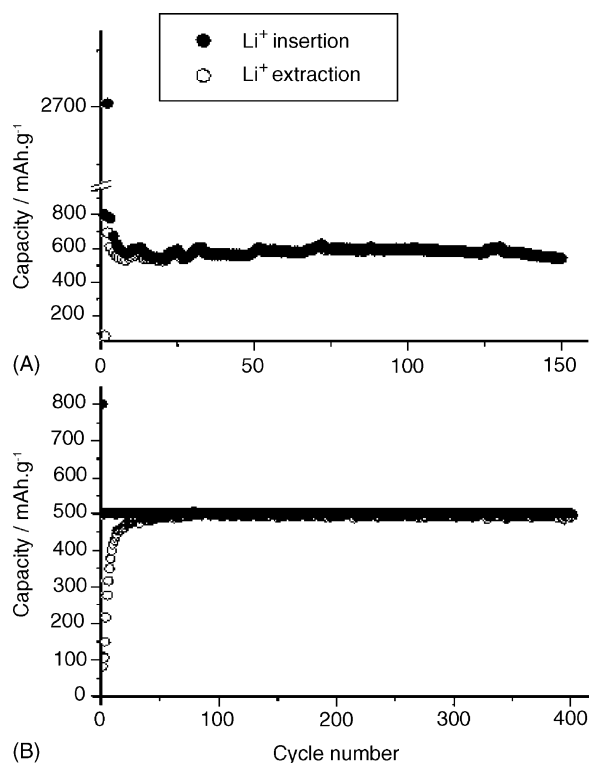


Fig. 6. Cycling test of Si:C (3:7) with addition of 10 wt% Ag composite anode, pasted on a nickel foam current collector. (A) Galvanostatic cycling at current density 0.5 mA cm^{-2} ($\approx 0.25 \text{ mA mg}^{-1}$) between 100 mV and 1.5 V. (B) Potentiostatic constant capacity (500 mAh g^{-1}) cycling at a current density 0.5 mA cm^{-2} ($\approx 0.25 \text{ mA mg}^{-1}$) between $\approx 70 \text{ mV}$ and 1.5 V.

tial cycles. Voltage profiles shown in Fig. 7 are also different for both types of current collectors. To shed more light on the processes that are involved in both configurations, differential capacity plots were recorded and shown in Fig. 8. Data were recorded for both copper and nickel foam composite electrodes cycled between 1.5 V and 40 mV versus Li. The shape of the peaks is slightly different in both cases. In the case of copper current collector, there are two distinguishable extraction peaks, located at ca. 380 and 510 mV. Increase in the cycle number leads to gradual decrease of peak area (extraction capacity). Peaks area ratio also changes. Area of the peak located at 380 mV increases while this at 510 mV decreases with cycles. The peak located at 510 mV can be assigned as Li–Si de-alloying. Peak at 380 mV is a result of contribution between carbon and silicon phases. Change of the ratio between these two peaks is an indication of a gradual change of the silicon phase with cycles, reducing its contribution to the overall electrochemical process. It is unexpected to see that the same material pasted on the nickel foam shows different behavior. During the initial cycles there is a low extraction peak (not shown for clarity), which corresponds to the low coulombic efficiency observed. As the cycling proceeds the extraction peak increases and between 20th and 100th cycles there is no considerable difference. This is probably related with the different SEI-film formation in both cases, al-

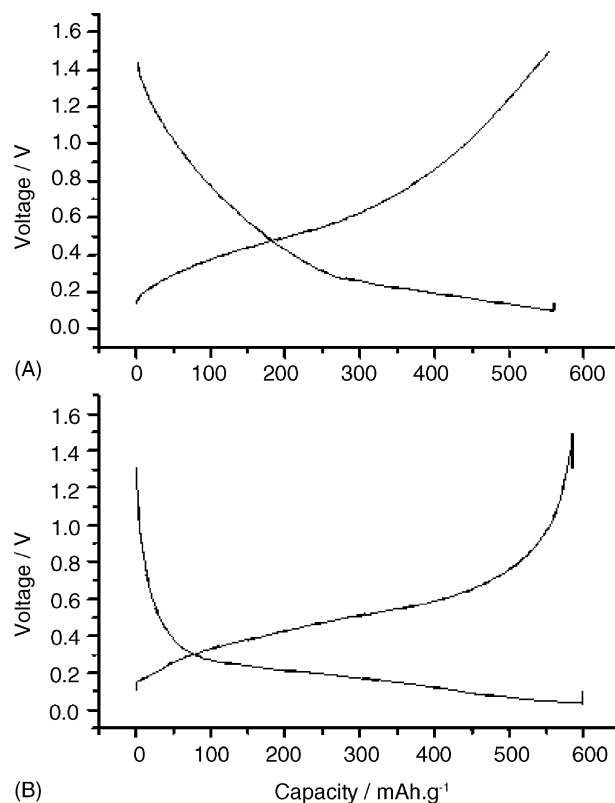


Fig. 7. Voltage profiles of Si:C(3:7) + 10 wt% Ag composite vs. Li metal. (A) Ni foam current collector; (B) copper foil current collector.

though the effect was not measured quantitatively. The large irreversible capacity loss in the case of nickel foam current collector suggests that there is probably an in situ film encapsulation of the active material that initially consumes large amount of Li^+ . A further understanding is still under way.

From a practical view point there is one more unfavorable feature of the nickel foam current collector, namely the low active material/current collector weight ratio. In the data presented in Figs. 5 and 6 the mass of the nickel foam was $\sim 100 \text{ mg}$ with active material on it only $\sim 5 \text{ mg}$, while in the case of $10 \mu\text{m}$ thin copper foil these values were, respectively, ca. 18 and 10 mg. We can easily estimate the required amount of the active material with a given capacity to reach some required capacity per unit electrode area. Most of the modern LIB's electrodes are constructed to deliver specific capacity of 2 mAh cm^{-2} or more. On the other hand, the Si/C composites might be used at various degrees of lithiation of the silicon phase. Higher specific capacity of the composite (i.e. higher degree of lithiation) would translate to a lower active material loading level (mg cm^{-2}) in order to reach the required capacity per unit electrode area as exemplified in Fig. 9. However, the cycle life of the mixed Si/C composite electrode is sensitive to both the degree of lithiation and the active material loading level. Lowering the both parameters generally give better results. Since the amount of 2 mAh cm^{-2} specific capacity should be always fulfilled, a tradeoff between the

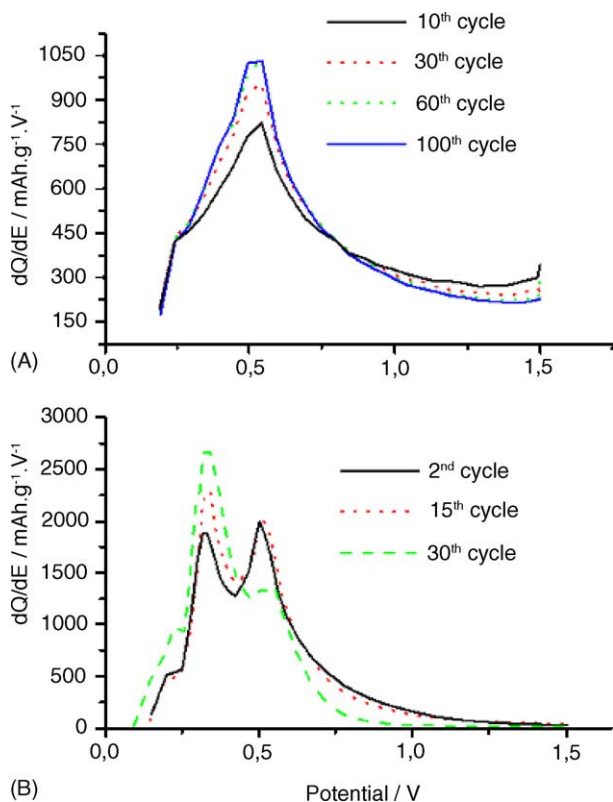


Fig. 8. Differential capacity plots of the mixed Si:C composite. Li-extraction peaks are plotted. (A) Ni foam current collector; (B) copper foil current collector. Peak area in (A) is smaller due to the smaller amount of the active material.

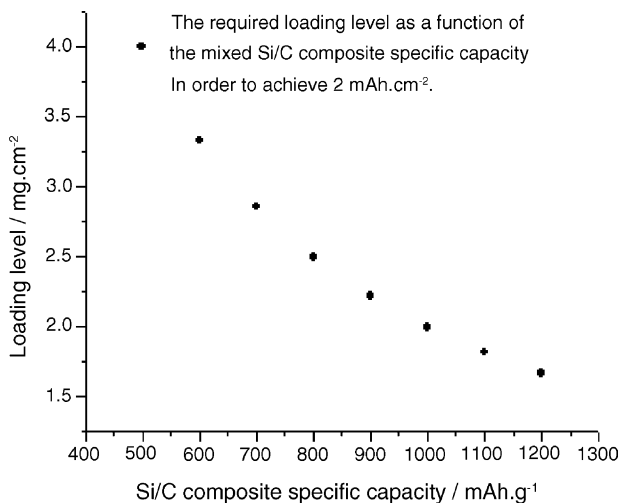


Fig. 9. The required active material load density vs. its specific capacity (degree of lithiation) in order to achieve 2 mAh cm^{-2} . Since the cycle life of the mixed Si/C composite electrode depends on the both parameters, an appropriate tradeoff between higher degree of lithiation and lower composite loading level is expected to be achieved.

degree of lithiation and the active material loading level is expected to be possible.

Despite of the aforementioned problems, these data are interesting from fundamental view point, showing that it could be possible to reach more than 100 cycles when using different electrode configuration by means of the standard slurry coating technique.

4. Conclusions

The silicon graphite mixed composites pasted on a nickel foam current collector demonstrated stable cyclic performance with high capacity. Composite was produced by means of a simple mechanical milling process. The copper foil current collector gives better active material/current collector weight ratio, but the microstructural changes (breathing) of the silicon particles finally lead to a macrostructural deformation of the electrodes. The latter is expected to be more severe in a spiral-wound battery construction. It therefore seems that the key step for improving of such composites could be sought in the alternative electrode configurations/textures which could be able to preserve the electrochemical reversibility despite of the microstructural changes that always accompany the Li–Si electrochemical alloying reaction.

References

- [1] A.M. Wilson, J.R. Dahn, J. Electrochem. Soc. 142 (1995) 326.
- [2] S. Bordearu, T. Brousse, D.M. Sleich, J. Power Sources 81–82 (1999) 233.
- [3] T. Yoshida, T. Fujihara, H. Fujitomo, R. Ohshita, M. Kamino, S. Fujitani, The 11th IMLB, Monterey, CA, USA, 2002 (Abstract no. 48).
- [4] H. Li, X. Huang, L. Chen, Z. Wu, Y. Liang, Electrochem. Solid State Lett. 2 (1999) 547.
- [5] G.A. Roberts, E.J. Crains, J.A. Reimer, J. Power Sources 110 (2002) 424.
- [6] Z.S. Wen, J. Yang, B.F. Wang, K. Wang, Y. Liu, Electrochem. Commun. 5 (2003) 165.
- [7] Y. Liu, K. Hanai, J. Yang, N. Imanishi, A. Hirano, Y. Takeda, Solid State Ionics 168 (2004) 61.
- [8] M. Yoshio, H. Wang, K. Fukuda, T. Umeno, N. Dimov, Z. Ogumi, J. Electrochem. Soc. 149 (2002) A1598.
- [9] N. Dimov, K. Fukuda, T. Umeno, S. Kugino, M. Yoshio, J. Power Sources 114 (2003) 88.
- [10] X.-Q. Yang, J. Mc Breen, W.-C. Yoon, M. Yoshio, H. Wang, K. Fukuda, T. Umeno, Electrochem. Commun. 4 (November) (2002) 893.
- [11] N. Dimov, S. Kugino, M. Yoshio, J. Power Sources 136 (2004) 108.
- [12] N. Dimov, S. Kugino, M. Yoshio, K. Fukuda, T. Umeno, 204th ECS Meeting, Orlando, FL, Abs 315.