Lithium insertion into Sn- and SnSb$_x$-based composite electrodes in solid polymer electrolytes

J. Yang [*], Y. Takeda, Q. Li, N. Imanishi, O. Yamamoto

Department of Chemistry, Faculty of Engineering, Mie University, Kamihama-cho, Tsu, Mie 514-8507, Japan

Abstract

Lithium insertion into Sn and SnSb$_x$ metallic hosts and the subsequent cycling behavior in polyethylene oxide (PEO)-based polymer electrolytes are examined. Inserted lithium can hardly be extracted from the electrode constituted by coarse tin powder due to the electrical isolation after dramatic host volume changes. Decreasing the host particle size and using intermetallic SnSb$_x$ alloy powders greatly enhance the electrode Li extraction capacity and its retention on cycling. The high irreversible capacity in the first cycle linked to the use of ultrafine host powders is compensated by introducing a certain amount of Li$_{2.6}$Co$_{0.4}$N into the electrode. Some factors influencing the cell performance are presented and discussed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Li-alloy composite electrodes; Solid polymer electrolytes; Lithium rechargeable battery; Cycling performance

1. Introduction

Lithium rechargeable batteries based on solid polymer electrolyte technologies have attracted worldwide attention. The development of polymer electrolyte systems is expected to result in an improvement of energy density and safety, and to enable a plastic configuration for enhanced versatility in battery design and reduced manufacturing costs. These new types of batteries are now being proposed for a wide variety of extremely demanding applications, such as electric vehicle, start–light–ignition and new types of electronic products.

However, some problems related to metallic lithium as anode have not been resolved. The high reactivity of the lithium metal to polymer electrolytes can lead to uncontrolled passivation phenomena [1,2]. As a result, dendrite formation and consequent cell short-circuiting are not eliminated. Generally, the presence of a trace amount of residual water and solvent can contribute to the observed instability of the lithium anode/polymer electrolyte interface [3]. A significant improvement in lithium interface has

been achieved recently by the use of true solid-state composite polymer electrolytes [4,5]. These battery systems have yet to demonstrate their long-term cycling stability.

No alternative lithium-source anode materials are available to replace lithium metal without sacrificing anode capacity and cell voltage. However, Li-alloy materials such as Li–Sn, Li–Al and Li–Si have demonstrated high charge density, decreased reactivity to electrolytes and rapid Li mobility in the alloys. They offer a promising alternative to lithium metal in polymer electrolyte-based systems. Some positive results have been obtained with Li–Al electrode [6] and interfacial layers of Li–Bi and Li–Pb alloys between the lithium metal and solid polymer electrolyte [7]. We focus our attention here on electrochemical behavior of lithium insertion into and extraction from Sn- and SnSb$_x$-based composite electrodes in polyethylene oxide (PEO)-based solid electrolytes.

2. Experimental

2.1. Electrode preparation

Tin (99.8%, < 45 μm) and nickel powder (99.9%, ca. 0.03 μm) were obtained respectively from Aldrich and

* Corresponding author. Tel.: +81-59-231-9419; fax: +81-59-231-9720.

E-mail address: nb7023d@cc.mie-u.ac.jp (J. Yang).

Nilaco. Sub-micron Sn powders (typical particle size < 1 μm) and Sn–Sb alloy powders (the nominal composition: $SnSb_{0.14}$ and SnSb, < 0.2 μm; the nominal composition: $SnSb_{0.17}$, < 1 μm) were prepared by chemical precipitation from aqueous solutions containing the reductive agent $NaBH_4$ and respective metallic salts in the presence of complexants such as citrates [8]. PEO, $LiCF_3SO_3$ salt and high-density polyethylene (PE, m.p. 144°C) were from Aldrich and $LiN(CF_3SO_2)_2$, denoted as LiTFSI, from Fluka. Composite electrodes were prepared by following two methods.

(1) A given weight of PEO (MW $= 9 \times 10^5$) and $LiCF_3SO_3$ were dissolved in acetonitrile under magnetic stirring. Metallic powders were then put into the viscous solution to form slurry. Ultrasonic generator was used to enhance the dispersion of the ultrafine metallic powders. The slurry was painted onto 280-mesh stainless steel grid. After solvent evaporation at 80°C, the samples were pressed by a pressure of 5 tons/cm^2 and finally dried at 115°C under vacuum for 2 h.

(2) PEO, polyethylene, inert conducting additive and active host powders were homogeneously mixed in agate mortar in glove box. The powder mixture was directly pressed onto the stainless steel grid. The electrodes containing highly active $Li_{2.6}Co_{0.4}N$ powder were prepared by this method.

All electrode composition was given by weight percent and the capacity was calculated according to the weight of active materials. The area of the composite electrodes was 0.65 cm^2 and the typical thickness was 45–55 μm.

2.2. Polymer electrolytes

A given weight of $LiCF_3SO_3$ (or LiTFSI) and PEO (MW $= 9 \times 10^5$) (O/Li $= 18$) were dissolved in anhydrous acetonitrile. After complete dissolution, the viscous solution was cast onto a Teflon dish under Ar atmosphere. Acetonitrile solvent was slowly evaporated in a glass desiccator under controlled N_2 gas flow. After complete evaporation, the film obtained was further dried at 90°C under vacuum. The film thickness was 90–100 μm.

2.3. Cell assembling

Cells consist of three parts: alloy composite electrode, two layers of the solid polymer electrolyte, which also acts as a separator, and 120 μm thick lithium counter electrode. The three different layers were stacked in stainless steel cell with rubber ring and metallic spring. A pressure was kept in the cells by means of the spring. The cells were assembled in glove box.

2.4. Electrochemical measurements

Before electrochemical measurements, the cells were preheated for 1 h at a temperature of 10°C higher than the operating temperature. For $LiCF_3SO_3$-containing electrolyte, the cell operation was at 80°C, for LiTFSI-containing electrolyte, at 75°C. Current density for cycling tests was 0.1 mA/cm^2. The rest time between charging and discharging was 1 min. Charging and discharging refer, respectively, to lithium extraction from, and insertion into metallic hosts. The impedance response was measured by Solartron SI 1260 (impedance/gain-phase analyzer) in a frequency range over 0.1 Hz and 10^6 Hz under an open-circuit condition.

3. Results and discussion

3.1. Granular and compositional structures of metallic host powders

Electrochemical lithium insertion into metallic hosts to form Li-alloys produces a drastic volume expansion. For example, the increase in volume from Sn to $Li_{22}Sn_5$ is 358%. During Li extraction, electrodes undergo a certain volume contraction. Such a strong volume effect could, on one hand, cause subdivision of host particles, poor inter-particle contacts and even disintegration of the Li-alloy-based electrode. On the other hand, when a composite electrode structure contains high-polymer electrolyte content, individual active particles are encapsulated by the polymer electrolyte and the composite structure can provide channels for ionic movement within the electrode. In this case, a direct interparticle contact is not absolutely necessary. However, the morphological changes can also cause poor contacts between active particle/polymer electrolyte interface and between the composite anode/the polymer electrolyte interface. As a result, rapid capacity fading and cycling instability take place during cell operation. This holds especially true for coarse metal host powder. Fig. 1 shows the first two discharge–charge profiles for a composite electrode based on coarse tin powder (particle size < 45 μm). The first lithium insertion produces three voltage plateaus, corresponding to different
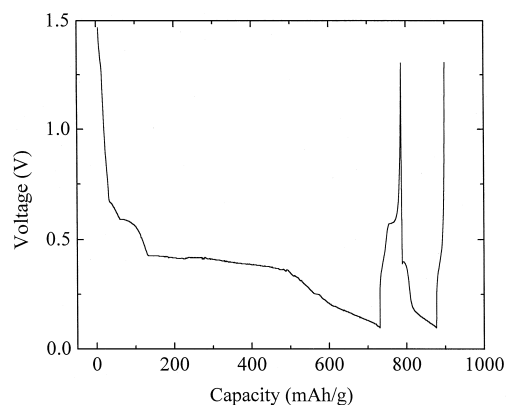

Fig. 1. The first two discharge–charge profile for the electrode based on coarse tin host powder in PEO–$LiCF_3SO_3$ electrolyte at 80°C. Electrode composition: 10% Ni, 10% PEO, 2% Li triflate and 78% Sn (< 45 μm).
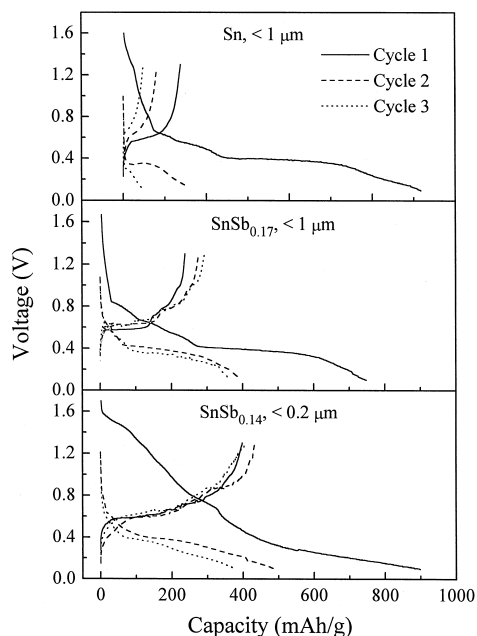
Fig. 2. Effect of the host structure and particle size on the initial cycles. Electrode composition: 15% Ni, 12% PEO, 3% $LiCF_3SO_3$ and 70% metallic host.

phase compositions. After lithium insertion, accommodated lithium can hardly be extracted from tin host and a further cycling is infeasible. The rapid electrode deactivation is attributed to electrical isolation of the active particles after the drastic volume changes.

To improve the electrode performance, it is necessary to alleviate the volume effect of the alloy system. This can be achieved by decreasing the host particle size and using multiphase alloy structure [9,10]. Several fine and ultrafine Sn and $SnSb_x$ powders were prepared for this purpose. Fig. 2 shows the influence of the granular and compositional structures on the electrode behavior. A little more lithium can be extracted from Sn host in the first cycle, when tin particle size is decreased from < 45 to < 1 μm. The capacity retention, however, remains poor. An improvement in the capacity retention can be achieved by the use of $SnSb_{0.17}$ (< 1 μm) alloy powder. As has been revealed [11], electrochemical Li insertion into $SnSb_x$ is performed in a stepwise mode, i.e., lithium is first inserted into SnSb phase at ca. 0.82 V vs. Li around still-ductile Sn phase. Such a Li insertion mode can buffer the electrode volume expansion effect and, therefore, improve the mechanical stability. With a further decrease in the host particle size (< 0.2 μm), Li extraction capacity can rise to 400 mA h/g for $SnSb_{0.14}$-based electrode. Finer host particles correspond to a smaller absolute volume expansion and have a weaker tendency to subdivision during cycling. Moreover, because the ultrafine powder possesses a relatively low packing density, its use can also reduce the relative volume change of the whole electrode. For these reasons, the mechanical stability and cycling capacity can be enhanced.

3.2. Polymer binder in composite electrodes

Drastic volume effect of metallic hosts during initial cycling requires choosing a suitable polymer binder. PEO polymer in the electrode functions as a binder. In addition, its combination with lithium salt can also provide channels for ionic movement within the electrolyte. As lithium is inserted into the host particles, the associated expansion stretches the polymer electrolyte, which undergoes a combination of elastic and viscous deformation. During the charging process, the alloy material will shrink in volume. Part of this will be accompanied by an elastic contraction of the polymer but the morphological changes induced by viscous flow may not be recovered. Continuous cycling of the insertion electrode may thus place considerable strain on the various interfaces that will influence the cell cycling stability. As shown in Fig. 3, the capacity is relatively low for the electrodes only using PEO polymer. This is, at least in part, attributed to not enough strong binding capability of the PEO. As the cell is operated at a temperature above the PEO melting point, the polymer is soft and viscous. A viscous flow of the PEO binder in the process of the volume changes of the alloy particles may be unfavorable for maintaining stable interface property and electrode morphology. A combination of two binders, soft PEO and rigid polyethylene (m.p. 144°C) together, gives higher cycling capacities. It is believed that the high-density polyethylene can improve the electrode morphology stability. However, when only polyethylene is used as binder, apparent voltage fluctuation takes place in the initial discharge process, implying an unstable interface contact. This seems to be linked to a lack of a cohesive interface connection due to high rigidity of the electrode at 80°C. Incomplete interfacial contact causes not only voltage in-
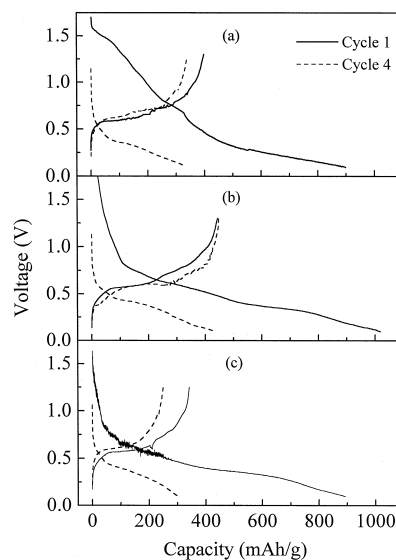

Fig. 3. Effect of polymer binder in the electrode on the cycle behavior. Electrode composition: (a) 15% Ni, 12% PEO, 3% $LiCF_3SO_3$ and 70% $SnSb_{0.14}$; (b) 15% Ni, 7% PEO, 5% PE, 2% $LiCF_3SO_3$ and 71% $SnSb_{0.14}$; (c) 10% Ni, 10% PE and 80% $SnSb_{0.14}$.
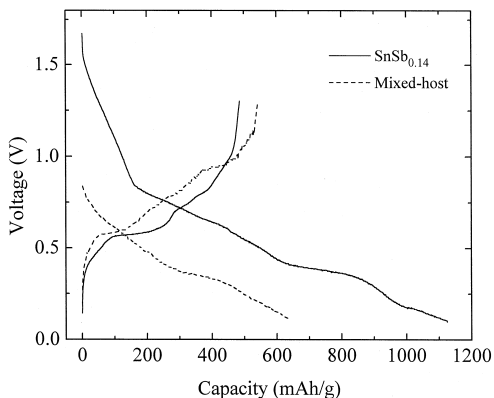
Fig. 4. A compensation for the $SnSb_{0.14}$ irreversible capacity in the first cycle by $Li_{2.6}Co_{0.4}N$. Electrode composition: (a) 12% Ni, 5% PEO, 7% PE and 76% $SnSb_{0.14}$; (b) 12% Ni, 5% PEO, 7% PE, 26.6% $Li_{2.6}Co_{0.4}N$ and 49.4% $SnSb_{0.14}$.
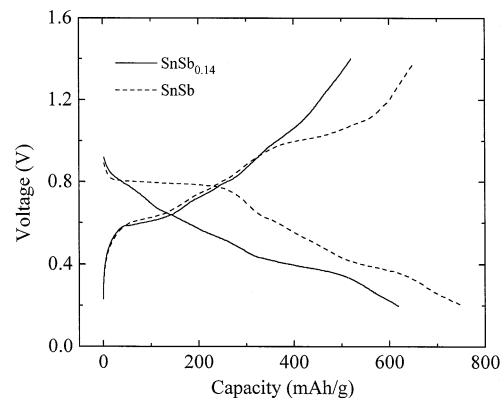

Fig. 6. The first discharge–charge profiles for the mixed-host electrodes with different alloy compositions in PEO–LiTFSI electrolyte at 75°C. Electrode composition: 12% Ni, 12% PEO, 8% PE, 20% $Li_{2.6}Co_{0.4}N$ and 48% $SnSb_x$.

stability, but also a degradation of the electrode performance. From this point of view, PEO as an electrode component is necessary.

3.3. Mixed hosts for composite electrodes

A disadvantage of the use of ultrafine host powders is the low coulombic efficiency in the first cycle (Fig. 3). The high irreversible capacity is mainly related to the formation of the surface film on the active particles, which arises from electrolyte decomposition reactions. Surface filming not only consumes charge for the irreversible reaction, but also increases the interfacial resistance and polarization. An effective approach to compensate the first irreversible capacity is adding a certain amount of

$Li_{2.6}Co_{0.4}N$ powder into the $SnSb_x$-based electrode. $Li_{2.6}Co_{0.4}N$ is known as a high capacity anode material for lithium ion cells [12]. Taking into account the high reactivity of $Li_{2.6}Co_{0.4}N$ compound to solvents, such a mixed-host composite electrode is prepared by direct powder-mixing and pressing method. Moreover, since lithium mobility in Li_x–$SnSb_{0.14}$ and $Li_{2.6}Co_{0.4}N$ is rapid at the cell operation temperature and, on the other hand, the solvent-free electrode preparation cannot ensure a homogenous salt dispersion in the electrode, the lithium salt will not be added into the dense composite electrodes to provide additional channels for ionic movement within the electrode.

Due to its low initial Li insertion capacity (< 100 mA h/g) but high Li extraction capacity (> 800 mA h/g), $Li_{2.6}Co_{0.4}N$ can play a role of an additional lithium source in this new type of electrode and, thereby, ensures a high efficiency in the first cycle as shown in Fig. 4. It is found, however, that this cell system has a poor capacity retention and cycling stability. Fig. 5 shows a comparison of the impedance changes in different polymer electrolytes during cell storage. The big and abnormal impedance change
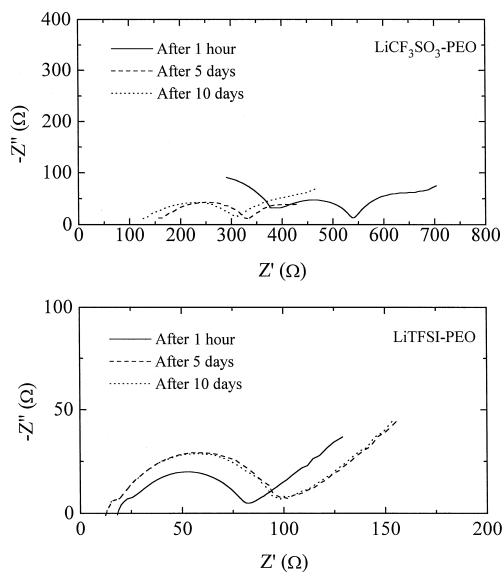

Fig. 5. Impedance changes during cell storage at 80°C. Electrode composition: 12% Ni, 8% PEO, 8% PE, 25.2% $Li_{2.6}Co_{0.4}N$ and 46.8% $SnSb_{0.14}$. Before storage, lithium was inserted into the mixed-host electrode until 0.1 V vs. Li.
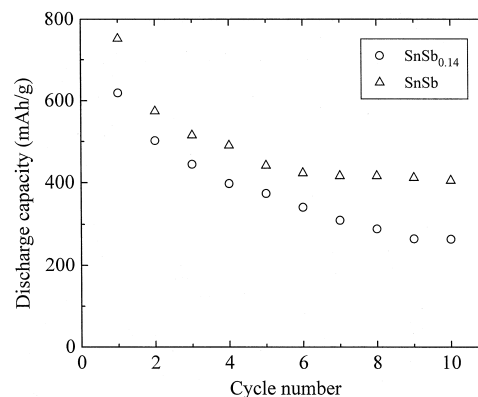

Fig. 7. Discharge capacity vs. cycle number for the mixed-host electrodes with different alloy compositions. The electrode compositions are the same as in Fig. 6.
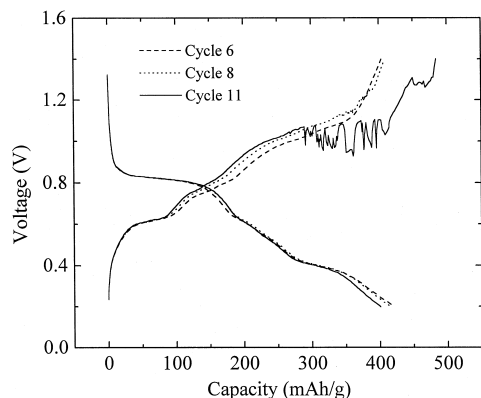
Fig. 8. Voltage instability in the charging process for a cell constituted by mixed-host electrode and lithium counter electrode at 75°C.

of the electrode in the $LiCF_3SO_3$-containing electrolyte indicates that the mixed-host composite electrode is not well compatible with the electrolyte. This may be a reason why the electrode performance decays quickly in this electrolyte. On the other hand, the LiTFSI-containing polymer electrolyte ensures a high ionic conductivity and a more stable interfacial property. In fact, the electrolyte films based on PEO and LiTFSI are soft and stick even at room temperature. This may be favorable for a cohesive and stable interfacial contact. Moreover, the small impedance change also indicates a good chemical stability between two different phases. For these reasons, the polymer electrolyte with LiTFSI, instead of with $LiCF_3SO_3$ salt, will be adopted for further study.

As mentioned above, $SnSb_{0.14}$ alloy as insertion material is superior over metallic tin. Figs. 6 and 7 show that this superiority is more apparent with increased Sb content in the Sn–Sb alloys. Li insertion into single SnSb phase can obtain a higher initial capacity and efficiency than into $SnSb_{0.14}$ two phase alloy (Sn + SnSb) under cut-off of 0.2/1.4 V. Moreover, its capacity retention is obviously improved. A long voltage plateau near 0.8 V for the electrode with SnSb powder in Fig. 6 represents Li insertion into SnSb phase to form Li_3Sb phase and highly around-dispersed Sn phase. After complete separation of SnSb phase, lithium is inserted into Sn phase, producing another two short voltage plateaus near 0.62 and 0.4 V. A further investigation on intermetallic SnSb phase recovery after Li extraction and its stability during cycling will be discussed somewhere else.

It is often observed that the voltage trend becomes unstable at the latter stage of the charging process after some cycles. Fig. 8 shows such a voltage instability after 10 cycles. This apparent voltage fluctuation is a typical sign of growing electrode disuniformities, such as lithium microdendrites [13]. The high cycling capacity easily promotes the formation and growth of the microdendrites on the lithium electrode. The dendrites could cause a shunt of a fraction of charging current, resulting in an excessively

high charge capacity as observed. The problem concerning lithium counter electrode interface greatly limits the feasibility for examining long-term cycling behavior of Li-alloy-based composite electrode. It is expected that a good cycling life performance could be achieved by the use of a suitable insertion cathode, in place of metallic lithium as counter electrode.

4. Conclusions

Lithium can be inserted into tin-based metallic hosts to form lithium alloys in PEO-based solid polymer electrolytes. The cyclability of the Li-alloy composite electrodes is strongly dependent on the host particle size and phase structure. The use of submicro $SnSb_x$ host powders greatly enhances the Li extraction capacity and its retention upon cycling. Adding $Li_{2.6}Co_{0.4}N$ into the $SnSb_x$-based composite electrodes can compensate the high irreversible capacity in the first cycle, which is related to the film formation on a large surface area of the ultrafine alloy powders. On the other hand, LiTFSI-containing polymer electrolyte is more matchable for the mixed-host composite electrodes than $LiCF_3SO_3$-containing polymer electrolyte. The cell cyclability is limited by the instability of lithium electrode interface. The high cycle capacity promotes the formation and growth of lithium dendrites on the lithium electrode. An excellent cycling stability requires choosing suitable insertion cathodes.

References

[1] F. Croce, B. Scrosati, J. Power Sources 43–45 (1993) 9.
[2] I.M. Ismail, U. Kadiroglu, N.D. Gray, J.R. Owen, in: Electrochemical Society Meeting Abstracts, San Antonio, TX, Oct. 6–12 Vol. 96-21999, Abstract 63.
[3] D. Fauteux, A. Massucco, M. McLin, M. Van Buren, J. Shi, Electrochim. Acta 40 (1995) 2185.
[4] G.B. Appetecchi, F. Croce, G. Dautzenberg, M. Mastragostino, F. Ronci, B. Scrosati, F. Soavi, A. Zanelli, F. Alessandrini, P.P. Prosini, J. Electrochem. Soc. 145 (1998) 4127.
[5] M. Mastragostino, F. Soavi, A. Zanelli, J. Power Sources 81-82 (1999) 729.
[6] A. Belanger, M. Robitaille, US Patent 4652506, 1989.

[7] M. Hiratani, K. Miyauchi, T. Kudo, in: Int. Conf. Solid State Ionics, Garmish 28–301988, p. 1431.

[8] J. Yang, M. Wachtler, M. Winter, J.O. Besenhard, Electrochem. Solid-State Lett. 2 (1999) 161.

[9] O. Mao, J.R. Dahn, J. Electrochem. Soc. 146 (1999) 423.

[10] J. Yang, Y. Takeda, N. Imanishi, T. Ichikawa, O. Yamamoto, J. Power Sources 79 (1999) 220.

[11] J.O. Besenhard, J. Yang, M. Winter, J. Power Sources 68 (1997) 87.

[12] Y. Takeda, M. Nishijima, M. Yamahata, K. Takeka, N. Imanishi, O. Yamamoto, Solid State Ionics, in press.

[13] B. Scrosati, R.J. Neat, in: B. Scrosati (Ed.), Application of Electroactive Polymers, Chapman & Hall, London-Glasgow-New York-Tokyo-Melbourne-Madras, 1993.