



PERGAMON

Electrochimica Acta 46 (2001) 1595–1603

ELECTROCHIMICA

Acta

www.elsevier.nl/locate/electacta

# XPS study of lithium surface after contact with lithium-salt doped polymer electrolytes

Iqbal Ismail<sup>1</sup>, Akihiro Noda, Atsushi Nishimoto, Masayoshi Watanabe\*

*Department of Chemistry and Biotechnology, Yokohama National University, Hodogaya-ku, Yokohama 240-8501, Japan*

Received 7 August 2000; received in revised form 3 October 2000

## Abstract

X-ray photoelectron spectroscopy (XPS) is used to probe the surface layer and element composition of Li-metal electrodes before and after contact with polymer electrolytes containing  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  (LiTFSI) or  $\text{LiBF}_4$ . Native film on as-received metallic lithium was composed of  $\text{Li}_2\text{CO}_3/\text{LiOH}$  in the outer layer and  $\text{Li}_2\text{O}$  in the inner layer.  $\text{LiF}$  was formed during lithium contact with electrolyte due to reaction between the native film and impurities in the electrolyte. The polymer electrolyte containing LiTFSI yielded a very thin film with limited porosity in the inner layers, which was reflected in the limited amplitude dependence of complex impedance spectra.  $\text{LiBF}_4$  mixed with polymer resulted in a thicker film with high porosity, as was postulated from the greater influence of the amplitude of the oscillation level. © 2001 Elsevier Science Ltd. All rights reserved.

**Keywords:** XPS; Polymer electrolyte; Lithium electrode; Passivation layer; Lithium polymer battery

## 1. Introduction

In order to improve the cyclability of lithium anode secondary batteries, the rechargeability of the lithium electrode needs to be improved. In other words, the compatibility of electrolyte with lithium metal must be enhanced, which means that a stable, low impedance interfacial layer is formed upon contact. It has been well known that the rechargeability problem is associated with the reactivity of the electrode when attached with electrolytes. It is proposed that the type of electrolyte is the main factor in controlling the nature of the passivation layer at the contact. Furthermore, investigations on the lithium anode suggest that the den-

dritic film formed on the anode during the cycling process strongly influences its rechargeability.

Due to the presence of organic and inorganic compositions at the surface of lithium metal after contact with electrolyte, surface analyses will complement the electrochemical studies. Beside several other techniques (e.g. FTIR [1], SEM [2]) X-ray photoelectron spectroscopy (XPS) has been widely used for studying the surface reaction of lithium electrodes.

In this study, we report the surface analyses of lithium electrode before and after contact with network polymer, NP, (prepared from mono-acrylated and tri-acrylated copolymer of ethylene oxide and propylene oxide) electrolyte membrane containing lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) or lithium tetrafluoroborate ( $\text{LiBF}_4$ ). The effect of different kinds of lithium salt on the electrode|electrolyte interface has been investigated using electrochemical and surface analysis methods. Models for the passivation layer are proposed, depending on the lithium salt incorporated in the membrane.

\* Corresponding author.

E-mail address: mwatanab@ynu.ac.jp (M. Watanabe).

<sup>1</sup> Permanent address: Department of Chemistry, King Abdul Aziz University, PO Box 9028, Jeddah 21413, Saudi Arabia.

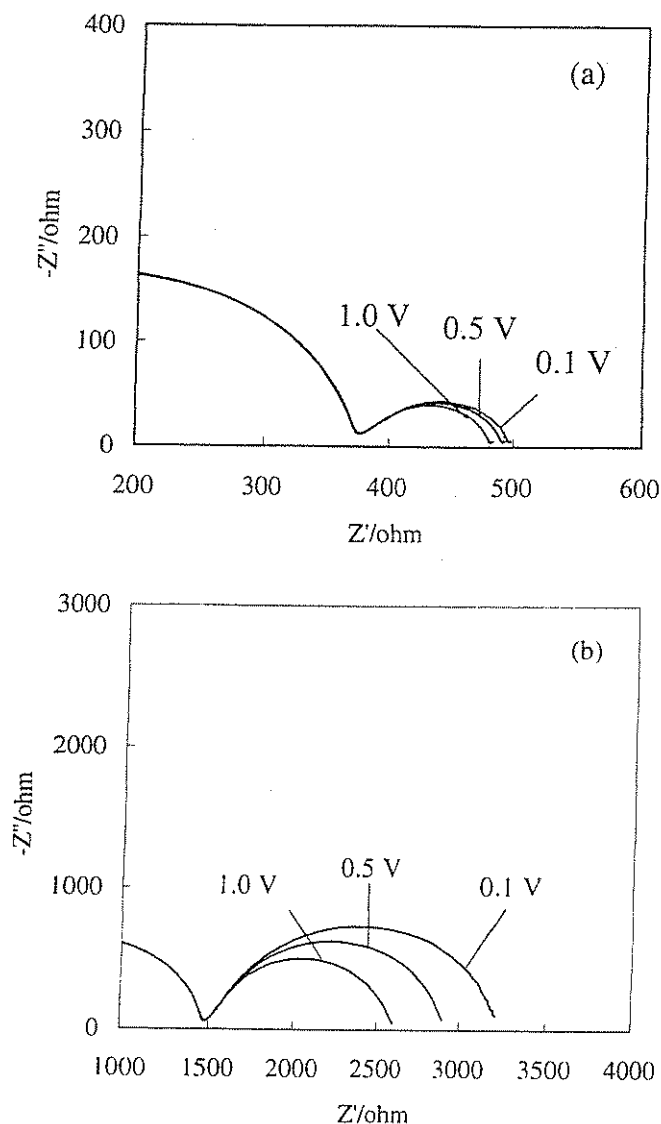


Fig. 2. Oscillation level dependence of impedance diagram for the network polymer complexed with (a) LiTFSI and (b) LiBF<sub>4</sub> and sandwiched between two symmetrical Li electrodes at 60°C.

trolytes containing LiTFSI or LiBF<sub>4</sub> ([Li]/[O] = 0.08) at 60°C. It is obvious here that LiTFSI-NP interface proved to be constant for a long time, whereas LiBF<sub>4</sub>-NP showed increasing interfacial resistance over the period of time. This is believed to be due to the instability of the latter salt.

Table 1 indicates data obtained from a Li/LiX-NP/Li (where X: TFSI<sup>-</sup> or BF<sub>4</sub><sup>-</sup>) electrochemical cell after 1 month of storage. The thickness of the passivation layer,  $l$ , was calculated using Eq. (1):

$$l = 2\pi f_{\max} \epsilon_r \epsilon_0 A R_i \quad (1)$$

where  $f_{\max}$  is the frequency at the maximum of imaginary part of interfacial impedance ( $-Z''$ ) in the complex

impedance diagram,  $\epsilon_r$  is the relative dielectric constant for the passivation layer, which was set at 10 for lithium compounds on the surface [5],  $\epsilon_0$  is the permittivity of vacuum, and  $A$  is the electrode area. Although a value of 5 was used [6] for  $\epsilon_r$  for an interfacial film between a highly lithiated cathode material in contact with tetraethylene glycol dimethyl ether, in the case of salted medium a higher permittivity value is more realistic. For simplicity, we assumed that  $\epsilon_r$  remained constant over the life of the interface while the passivation thickness varied. The estimation of film thickness in this work is much smaller than that reported by Sloop and Lerner [7], who estimated the thickness after 1 week of lithium metal contact with poly(ethylene oxide)/LiClO<sub>4</sub>. This may be due to low water content (< 20 ppm) in our polymer electrolytes.

Passivation film thickness values for lithium after contact with LiTFSI-NP and LiBF<sub>4</sub>-NP, are lower and higher, respectively, if compared with that calculated for the film formed on Li metal in contact with a linear polyether (tetraethylene glycol dimethyl ether) [8]. This wide variation in film thickness associated with lithium salt type suggests that the polymer host has a less significant role in controlling the interfacial property, and the nature of lithium salt has a greater effect in modifying the structure of the passivation layer.

It can be noticed here that the thicker interface for LiBF<sub>4</sub>-NP is associated with higher resistance, lower capacitance and larger time constant. This greater rise in  $R_i$  for LiBF<sub>4</sub>-NP, compared with the LiTFSI-NP, is another indication of the contrast in the nature of the interface between the two cases. Fig. 2 shows the amplitude dependence of impedance response for (a) LiTFSI-NP and (b) LiBF<sub>4</sub>-NP. It can be seen here that, in both compositions, the high frequency semi-circle is the same for different amplitudes. The high frequency semi-circle agreed well with that obtained when blocking, stainless steel, electrodes were used (not shown here). This indicates that the resistance for the high frequency semi-circle corresponds to the bulk property of the polymer electrolyte. However, the low frequency semi-circle depicted different behavior for the two salt compositions. LiBF<sub>4</sub>-NP was remarkably dependent on the amplitude, whereas LiTFSI-NP was not greatly influenced.

### 3.2. XPS analysis for the native film on the lithium surface

Fig. 3 shows the XPS spectra of Li 1s, C 1s, and O 1s regions for the native film on the lithium surface. In these spectra, three lithium compounds are observed, i.e. Li<sub>2</sub>CO<sub>3</sub>, LiOH and Li<sub>2</sub>O. The peak at 55.2 eV in Li 1s region can be assigned to Li<sub>2</sub>CO<sub>3</sub> and/or LiOH,

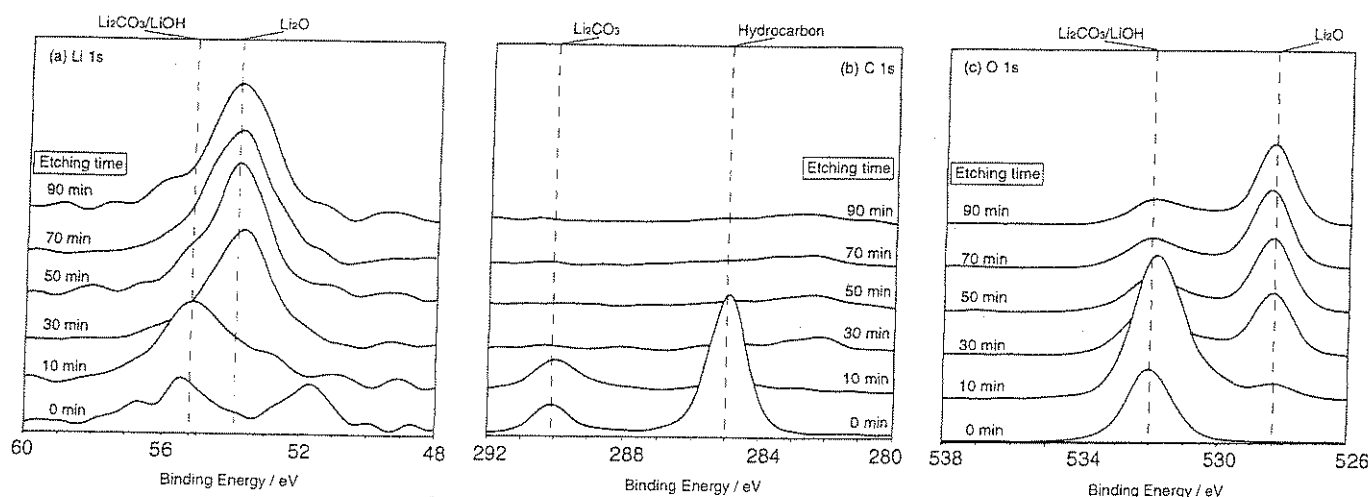


Fig. 3. XPS spectra for the native film on as-received Li-foil.

whose intensity decreases with etching time. The peak at 54.0 eV corresponding to  $\text{Li}_2\text{O}$  is observed after 30 min of etching time and is detectable up to 90 min of etching time with almost the same intensity. It may be noticed that the thickness of the native film on lithium foil was estimated by Kanamura et al. [9] to be as much as 900 Å. However, due to instrumental limitation in this work we were unable to extend the argon ion sputtering time and thus, no peak for Li metal (at  $\sim 52.3$  eV in Li 1s) was possible to detect. Nevertheless, we do not expect that the native film in our work is that thick, since during cell assembly for electrochemical measurements lithium foil was firmly pressed on the stainless steel substrate in order to break the native film on the lithium surface. A similar treatment was applied prior to XPS measurement for the as-received lithium surface.

Fig. 3b shows C 1s peaks for the native film on as-received lithium foil. A sharp peak of hydrocarbon is depicted at 285.0 eV before etching, as usual. Hydrocarbon is believed to exist in the glove box and/or the XPS chamber as a contaminant, which is mainly adsorbed on the outer surface of the sample. The peak at 290.1 eV corresponding to  $\text{Li}_2\text{CO}_3$  is observed in the outer layer of the native film and up to 10 min of etching time in a greater intensity, though in the following scans its intensity decreases remarkably. Fig. 3c shows XPS spectra of the O 1s region. A peak at 532.0 eV corresponding to  $\text{Li}_2\text{CO}_3/\text{LiOH}$  is observed, which also decreases after 10 min of etching time. A small peak, but with strong intensity later, appears at 528.3 eV corresponding to  $\text{Li}_2\text{O}$  at 10 min of etching time. The above analysis indicates that the carbonate layer is relatively thinner when compared with the oxide layer. These observations for  $\text{Li}_2\text{CO}_3/\text{LiOH}$  and  $\text{Li}_2\text{O}$  in Li 1s, C 1s, and O 1s spectra, are in good agreement with each other in terms of etching profile in accordance with their assigned compositions. The native film on the

as-received lithium can be described schematically as in Fig. 4.

### 3.3. XPS analysis for the lithium surface following contact with polymer electrolytes

Fig. 5a–d show the XPS spectra of Li 1s, C 1s, O 1s, and F 1s regions for the lithium surface following contact with LiTFSI-NP. It may be noticed that peak positions are displaced, compared with those of native film spectra. This is because different calibrating peaks are used for the before and after contact samples (see Section 2). In Fig. 5a  $\text{Li}_2\text{CO}_3/\text{LiOH}$  peaks are apparent from 16 min of etching time onward, whereas the peak assigned to  $\text{Li}_2\text{O}$  starts to appear from 36 min of etching time. The TFSI anion or polymer electrolyte peak is observed at 286.8, 533, and 689.2 eV in C 1s, O 1s, and F 1s regions, respectively, before etching and decreased thereafter. This organic content at the surface is the undetached part of the electrolyte left while peeling it off from the electrode and/or it is the product of reaction between the electrolyte and metallic lithium. At 16 min of etching time onward, a peak at 283.8 eV in the C 1s spectrum is recorded which corresponds to the carbide. Fig. 5a and d present the LiF peak at 56.0 eV in Li 1s and 685.5 eV at F 1s regions, respectively.

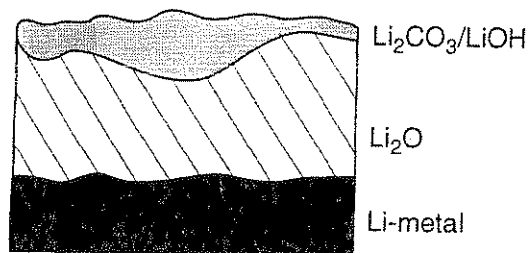


Fig. 4. Schematic illustration for the native film on as-received Li-foil.

outer layer. Thus, we believe that the TFSI<sup>-</sup> peak observed on the outer layer is its natural form rather than the polymeric product, and therefore, the only source for LiF is the acid–base reaction between HF and the lithium compounds in the native film.

Fig. 6a–d show the XPS peaks of Li 1s, C 1s, O 1s, and F 1s regions for the lithium surface following contact with LiBF<sub>4</sub>-NP. In Li 1s (Fig. 6a) and F 1s (Fig. 6d) spectra it may be seen that LiF is formed on the surface with increasing intensity in the following spectra as a function of etching time. Li<sub>2</sub>CO<sub>3</sub>/LiOH peaks are observed in Li 1s (Fig. 6a) and O 1s (Fig. 6c)

spectra, i.e. almost from 0 to 36 min of etching. The Li<sub>2</sub>O composition peak starts to appear at 16 min of etching time in O 1s (Fig. 6c), which showed an increasing trend thereafter. A polymer peak is observed in the outer layer at 286.8 and 533 eV in C 1s (Fig. 6b) and O 1s (Fig. 6c), respectively. No peak for adsorbed BF<sub>4</sub> in the F 1s spectra, no seen in Fig. 5, is apparent.

### 3.4. Depth profiles of the lithium surface

Fig. 7 shows a depth profile for each element in the surface film of lithium as received (a) and after contact

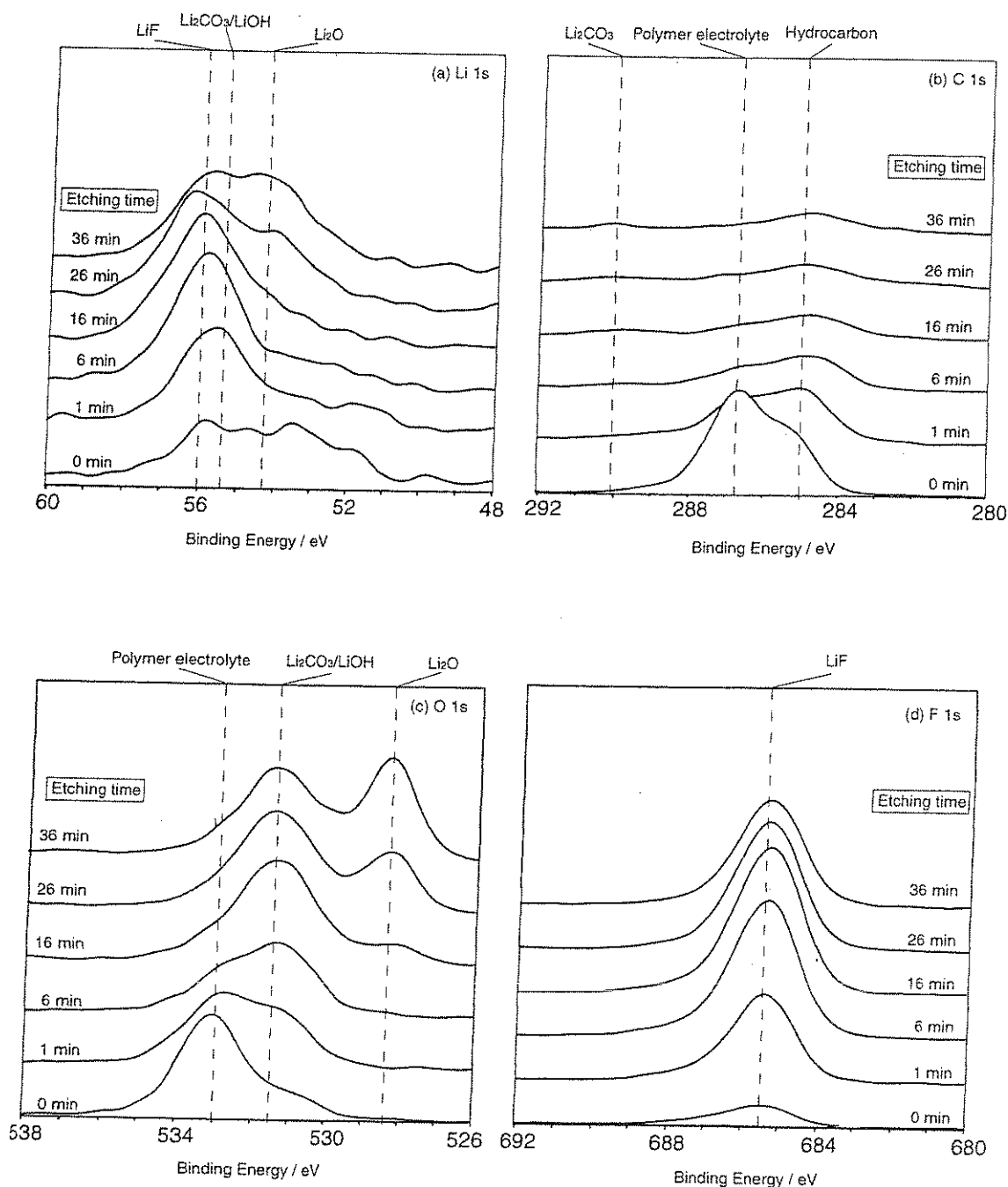


Fig. 6. XPS for Li-foil after 1 month of contact with LiBF<sub>4</sub>-NP at 60°C.

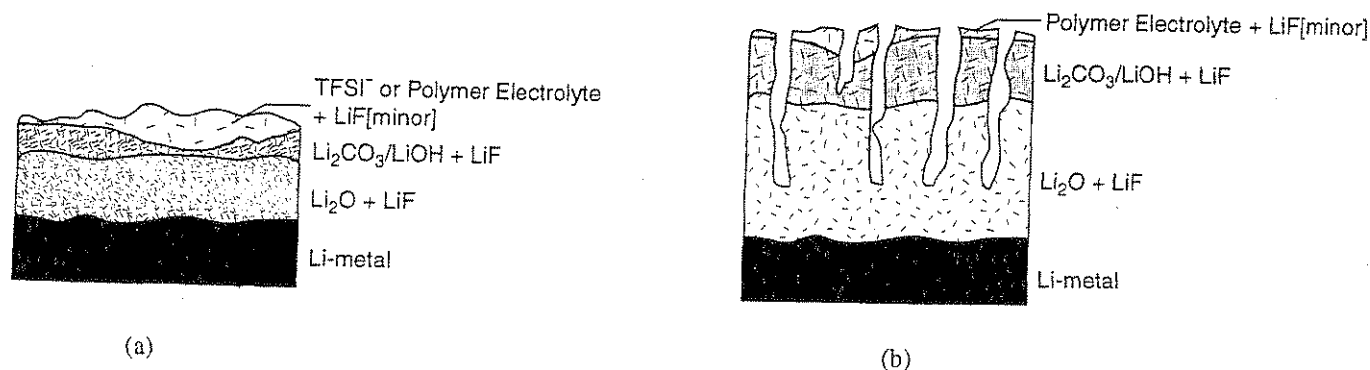


Fig. 8. Schematic illustration for the surface film formed on the Li-foil after contact with (a) LiTFSI-NP or (b) LiBF<sub>4</sub>-NP.

### Acknowledgements

This research was supported in part by Grant-in-Aid for Scientific Research on Priority Areas (A) 'Molecular Synchronization for Design of New Materials System' (No. 404/11167234) from the Japanese Ministry of Education, Science, Sports, and Culture, and NEDO International Joint Research Grant. The authors would like to thank Dr. M. Kondoh for taking XPS measurements of the Li samples and Dr. Kiyoshi Kanamura, Tokyo Metropolitan University, for a useful discussion. The authors would also like to thank Dai-ichi Kogyo Seiyaku for supplying them with valuable macromonomers. I.I. would like to thank Japan Petroleum Institute and Petroleum Energy Center (Japan) for financial support.

### References

[1] D. Aurbach, B. Markovsky, M.D. Levi, E. Levi, A.

- Schechter, M. Moshkovich, Y. Cohen, *J. Power Sources* 81-82 (1999) 95.
- [2] K. Kanamura, S. Shiraishi, H. Tamura, Z. Takehara, *J. Electrochem. Soc.* 141 (1994) 2379.
- [3] M. Kono, E. Hayashi, M. Watanabe, *J. Electrochem. Soc.* 146 (1999) 1626.
- [4] M. Kono, E. Hayashi, M. Nishiura, M. Watanabe, *J. Electrochem. Soc.* 147 (2000) 2517.
- [5] K.A. Murugesamoorth, J.R. Owen, *Br. Polym. J.* 20 (1988) 227.
- [6] P.G. Bruce, F. Krok, *Electrochim. Acta* 33 (1988) 1669.
- [7] S.E. Sloop, M.M. Lerner, *J. Electrochem. Soc.* 143 (1996) 1292.
- [8] A. Lisowska-Oleksiak, *Solid State Ionics* 119 (1999) 205.
- [9] K. Kanamura, H. Tamura, S. Shiraishi, Z. Takehara, *J. Electrochem. Soc.* 142 (1995) 340.
- [10] K. Kanamura, H. Tamura, Z. Takehara, *J. Electroanal. Chem.* 333 (1992) 127.
- [11] K. Naoi, M. Mori, Y. Naruoka, W. Lamanna, R. Atanasoski, *J. Electrochem. Soc.* 146 (1999) 462.