Short communication

Effect of the atmosphere on chemical composition and electrochemical properties of solid electrolyte interface on electrodeposited Li metal

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ABSTRACT

Many efforts have been paid to realize the superior anodes for future Li batteries in either the dry Ar atmosphere or the dry air atmosphere. In this work, in order to clarify the effects of such atmospheres, the most reactive anodes of Li were freshly electrodeposited under the dry Ar or under the dry air condition. The Solid Electrolyte Interface (SEI) formed during the electrodeposition of Li anodes is revealed to have a different chemical composition and protective feature. The Li deposited under the dry air was revealed to have longer cycle life in the electrolyte than that deposited in Ar, even in the electrolyte containing ionic liquid. From the XPS results, the SEI formed in dry air is proved to be different from that formed in Ar gas atmospheres, that is, the SEI formed in dry air consists of Li_2CO_3 and Li nitride. In order to improve the performance of the anodes, the atmosphere for the initial preparation of the anode/electrolyte interface should be tuned.

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1. Introduction

Li ion batteries are now the key electric power supplies for small electronic equipment, and Li ion batteries are going to be used for hybrid and electric vehicles. Many researchers are attracted to improve the energy density, power density, as well as safety and the longer cycle life of the Li ion batteries. On the other hand, the alloys with Li and the metallic Li are the other candidates to realize higher energy density batteries, and many researchers paid efforts to apply those metallic anodes to the batteries.

Some of the approaches to realize such anodes are the selection of the electrolyte solution and the adequate additives and the selection of solvent. Due to their quite cathodic potential, Li alloys and the metallic Li anode, by the contacting the electrolyte, a Solid Electrolyte Interface (SEI) is formed on the surface of the anode by the decomposition of the electrolyte molecules. The stability of the SEI leads to longer cycle life, and the Li^+ permeability in the SEI is one of the dominant factors for the interfacial resistance during the electrochemical reaction. With coherent SEI film, Li metal can be electrodeposited without the dendritic deposition preventing the continuous side reaction during the charge–discharge cycling in the battery operation. In order to understand high performance batteries, it is important to learn about the characteristics of the SEI layer.

The performance of anodes while varying the electrolyte systems and the additives is investigated under the atmosphere of dry Ar or that of dry air. There are many reports on the performance of metallic Li anode [1–4] or other anodes [5,6] in the Ar atmosphere. Also, there are some reports on the characterization of Li metal anodes in dry air atmosphere [7,8]. In the dry air atmosphere, Li metal ribbon seems to be stable, because of the nature of film formed by storage in dry air, while the fresh surface of Li metal reacts with O_2 or N_2. In those reports, sometimes there is a lack of discussion on the effect of atmosphere, especially the effect of dry air. It is also reported that the specific treatments of carbon in dry air leads to changes in surface condition and improves anode performance [9]. Also an addition of CO_2 into the electrolyte system of propylene carbonate with $LiClO_4$ is known to lead to superior performance for the electrodeposited Li anode [10].

In this study, the performances of Li metal anodes electrodeposited either under dry Ar or under dry air were investigated. In order to clearly make the difference and avoid the effect of the native film on Li having hysteresis, freshly electrodeposited Li was selected to be examined by an evaluation of the morphology, the chemical composition and the charge–discharge performance.

2. Experimental

The assembly and evaluation of the electrochemical cells were operated either under the dry Ar atmosphere in Ar filled glove box with dew point below −90 °C (<0.1 ppm of H_2O), which equipped with de-humidifier of Ar, or in the dry-room with dew point of

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below −80 °C of supplying air and −60 °C (<10 ppm of H_2O) at the discharge air.

The test samples of freshly deposited Li on Ni foil were obtained with 2.0 mA cm^{-2} of cathodic current with 5.1 C cm^{-2} of charge in 1 mol dm^{-3} LiPF$_6$/ethylene carbonate (EC)-diethyl carbonate (DEC) (50:50, vol.%) with less than 20 ppm H_2O content purchased from Kishida Chemical Co., Ltd. Li foils were used for the reference and counter electrodes.

The morphology of the electrodeposited Li anodes was observed by the field emission-scanning microscope (FE-SEM). The chemical condition of the Li surface was characterized by X-ray photoelectron spectroscopy (XPS) with Ar$^+$ etching. All of the samples were washed by pure dimethyl carbonate, dried under a vacuum, and transferred to the chambers under Ar atmosphere.

The accelerated charge–discharge cycle test of the deposited Li metal anode was conducted according to the procedure previously reported [11], followed by the electrochemical deposition of Li. In each cycle, Li was dissolved/deposited with 1.0 C cm^{-2} with 2.0 mA cm^{-2} of the loading current. When the potential reached to 1.0 V vs. Li/Li$^+$ during the discharge, the dissolution/deposition cycle was terminated. As for the reactive additives for the electrolyte to evaluate the protective performance of SEI, 1-butyl-1-methylpyrrolidinium (BMP) bis(trifluoromethylsulfonyl)imide (TFSI), 1-ethyl-3-methylimidazolium (EMI) TFSI, or 1,3-diallylimidazolium(DAI) TFSI (Toyo Gosei Co., Ltd.) were added.

3. Results and discussion

In this study, we have selected the loading current density for deposition and dissolution of Li as 2.0 mA cm^{-2}. From the results in our previous study, we have been noticed to adopt 1.0 mA cm^{-2} of loading current lead adequate performance for Li metal anode [10,11], in this study, we applied higher current of 2 mA cm^{-2} to bring the Li metal anode in a severe condition to emphasize the protective characteristics of SEI on Li anode. The morphology of the electrodeposited Li is shown in Fig. 1. Both of the Li anodes deposited under Ar or dry air are found to have flake shaped grains. The Li deposited under Ar had a rough surface with pores, which indicated the heterogeneity of the Li deposition site. On the other hand, the Li deposited under the dry air had less pores, as indicated the uniformity of Li nucleation during the electrodeposition. It is well known that the surface condition of Li strongly influences the morphology. Choi et al. reported the morphological change of the electrodeposited Li by the surface treatment [12]. The nature of the electrolyte also influences the surface morphology of the electrodeposited Li, as reported by Ota et al. [13]. In the case of this work, Li was electrodeposited in the same electrolyte solution of 1 mol dm^{-3} LiPF$_6$/EC-DEC, while the soluble gas from the dry air is the only difference during the electrodeposition. The ionic conductivity of the electrolytes was identical, which creates no differences in the current distribution during the deposition. It is considered that the difference of the SEI formed on the Li surface during the deposition would cause the morphological difference. An inhomogeneous distribution of the reaction site may result in rough morphology compared with the homogeneous growth of Li in the vertical direction under coherent SEI, which leads to the flat surface of the deposit.

The SEI layer was investigated by XPS analysis with use of Ar$^+$ etching. The XPS spectra of the most upper part of the SEI was obtained, and then Ar$^+$ etching was performed followed by the acquisition of XPS spectra for the study of the inner part of the SEI. The preliminary study revealed that even after the 600 s Ar$^+$ etching, Li metal does not appear by observing the Li 1s sector at 52.0 eV. Fig. 2 illustrates the XPS spectra of Li 1s, C 1s, O 1s and N

1s for the SEIs on Li metals deposited in either the Ar or dry air atmosphere before and after the Ar$^+$ etching of 400 s.

The XPS spectra of each element at the most surface part, i.e. the spectra obtained before Ar$^+$ etching, for the Li deposited in Ar and the Li deposited in dry air, are identical. This suggested the top parts of both of the SEI layers having a similar chemical structure, while, the spectra obtained from the inner part of those SEI layers after 400 s Ar$^+$ etching revealed quite different features.

In the XPS spectra before Ar$^+$ etching, peaks of Li 1s shifted to the positive side from Li metal 52.0 eV to around 55.3 eV. This peak shift appearing close to 55.5 eV revealed that the surface of SEI consisted of Li$_2$CO$_3$ and/or LiOH [14,15]. After Ar$^+$ etching, peaks of Li 1s in the spectrum obtained from Li that deposited in Ar seemed to shift slightly to lower binding energy while broadening at the same time. On the other hand, the Li 1s peak of the etched Li deposited in dry air showed a strong level of intensity compared with Li deposited in Ar, with a shoulder around 53.7 eV, which is assigned to be Li$_2$O [15], while the main peak of Li 1s stayed almost the same 55.2 eV as before the Ar$^+$ etching. From the result, the amount of the Li element in the inner part of the SEI formed in dry air is considered to be larger than that of the SEI formed in Ar. The broadening and shoulder of Li 1s peak in the spectrum in the etched SEIs deposited in Ar and deposited in dry air is considered to be due to the existence of Li$_2$O as well as Li$_2$CO$_3$ and/or LiOH in the inner part of SEI.

The spectra of C 1s of SEI deposited in dry air showed identical properties with those deposited in Ar, for either the most upper part or the inner part of SEIs. The spectra of the C 1s signal revealed that the chemical condition and amount of C element at the most upper part of SEI is quite different compared with the inner part. At the surface, in both cases of SEIs formed either in Ar or in the dry air large peak appeared around 284.0 eV which is assigned to hydrocarbons. Reducing the decomposition of the solvent is considered to result in the deposition of hydrocarbons in SEI on Li. In the inner part of SEIs, the two peaks at 284.0 eV and around 281 eV appeared. The C 1s signal of around 281 eV of binding energy is considered to be the photoelectron from metal carbide [15]. The signal around 281 eV also appear in the spectra of samples before etching as shoulders. This consideration leads to the possibility of the existence of Li–C bonding.

As shown in Fig. 2c, the O 1s spectra of the upper part of SEIs, formed in either Ar or dry air, are identical. In those spectra a O 1s peak appeared around 534.0 eV, which attributed to the oxygen with –C=O or –C–O– bonding [14,15]. After etching, another peak around 531.5–532.0 eV appeared. This signal revealed the existence of Li$_2$CO$_3$ in the inner part of SEIs in both SEIs formed in Ar or dry air, while the amount of Li$_2$CO$_3$ in the SEI formed in dry air is considered to be much larger than that formed in Ar with consideration of the signal ratio. The result from O 1s spectra shows good agreement with that from Li 1s spectra.

The spectra of N 1s, clearly revealed a difference between the SEI formed in Ar and that formed in dry air. Before Ar$^+$ etching, the N 1s spectra showed peaks with a weak intensity around 399 eV. These are considered to be due to the N$_2$ trace in the XPS chamber by transferring the sample in. On the other hand, a peak with a strong intensity at 403.5 eV appeared only in the inner part of SEI formed in dry air. The binding energy of N 1s around 403 eV is considered to be one of nitrogen consisting of metal nitride. The only potential compound of metal nitride in this system is Li$_3$N [16]. Li$_3$N and LiOH are supposed to form by chemical reaction with Li similar mechanisms proposed by Wang et al. [17].

From the results, the chemical composition of the SEI of Li formed by electrodeposition is considered as follows. The top surface of SEI formed in Ar has hydrocarbons which is a resultant product of the reducing decomposition of solvents. The inner part of SEI formed in Ar consists of Li$_2$CO$_3$ and/or LiOH as well as hydrocarbons. On the other hand, SEI formed in dry air has a similar

a) Deposited in Ar

b) Deposited in dry air
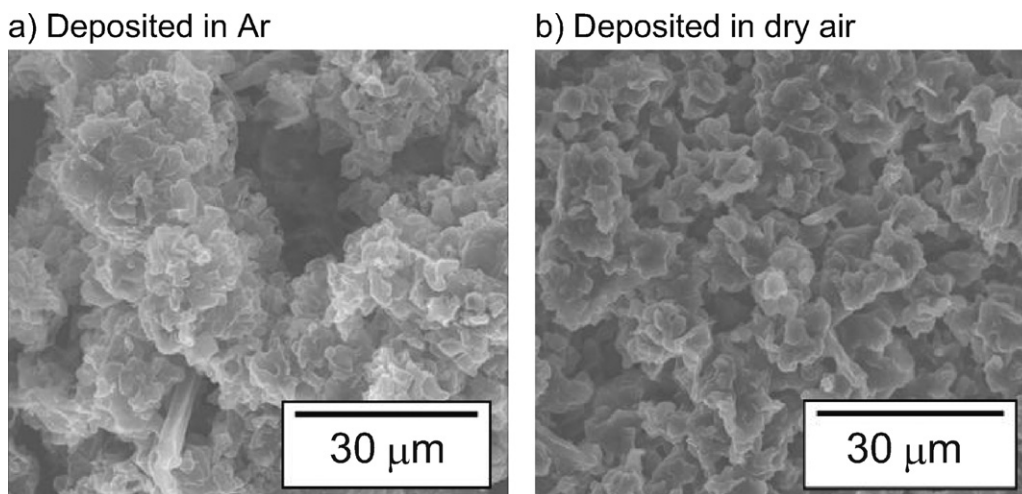


Fig. 1. Surface morphology of the Li anodes deposited in (a) dry Ar or (b) dry air. The current density for the electrodeposition was $2.0\,\mathrm{mA\,cm^{-2}}$ with $5.1\,\mathrm{C\,cm^{-2}}$.

composition at the top surface, while the inner part of the SEI formed in dry air also has hydrocarbons, a larger amount of Li_2CO_3 and/or LiOH compared to that formed in Ar and, in addition, a considerable amount of Li_3N.

The charge–discharge cycling test to check the cycle stability proposed by Koch [18] revealed the differences of the electrochemical reaction of Li at the interface between the SEI and the Li surface. As we described, in this study, we have selected the loading current density as $2.0\,\mathrm{mA\,cm^{-2}}$ to revealed the protective characteristics of

SEI on Li anode. Fig. 3 illustrates the potential-time profile during the constant current dissolution/deposition cycling test. During the cycling, the electrode potential in the discharging process showed an increase after a certain cycling, which represented the exhausting excess amount of Li by the consumption of charging current for the side-reaction or consumption of Li metal by a chemical reaction with electrolyte. The cycling tests for the Li anodes formed in various atmospheres were performed, and the results are shown in Table 1. It is clear that the Li deposited in the dry air atmosphere
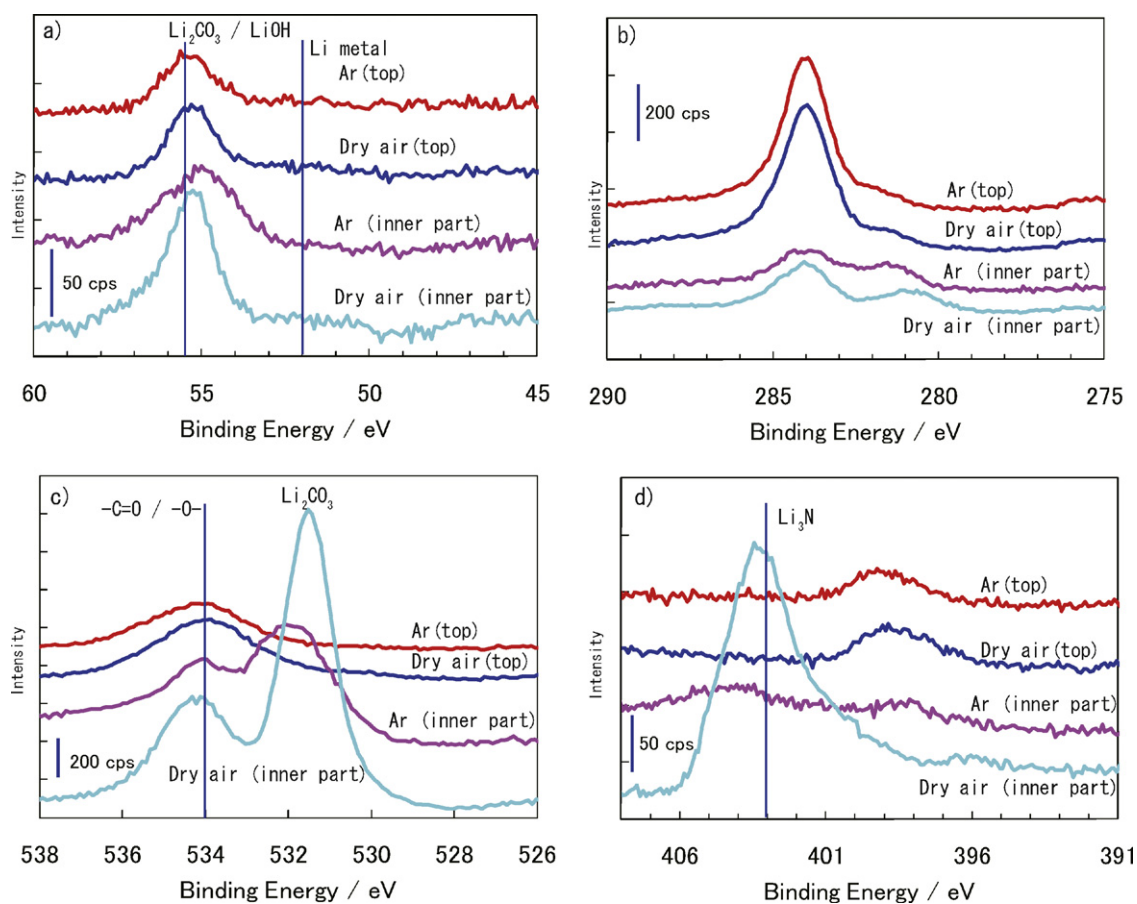
Fig. 2. XPS spectra of the Li anodes deposited in Ar or dry air. The XPS spectra were obtained as the dried state and after Ar^+ etching for 400 s. The spectra of Li 1s, C 1s, O 1s, and N 1s are shown in (a), (b), (c) and (d) respectively.
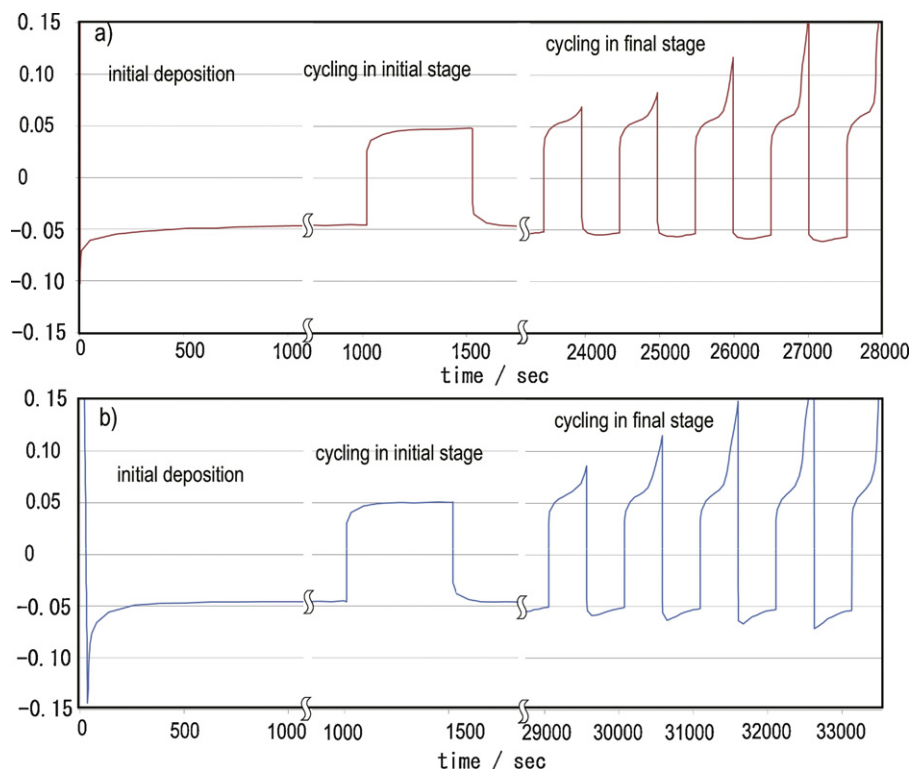
Fig. 3. Potential profile during the initial deposition of Li and following constant current charge–discharge test of electrodeposited Li anodes operated under Ar (a) or dry air (b). The initial deposition charge of Li was $5.1\,C\,cm^{-2}$. The charge amount of $1.0\,C\,cm^{-2}$ were passed for each charge and discharge step. The loaded current density was $2.0\,mA\,cm^{-2}$.

has a higher cycling number, i.e., a higher current efficiency than that of Li deposited in Ar. The SEI formed on the Li anode in dry air seems to have a protective layer against the side reaction during the dissolution/deposition reaction of the anode. In addition, the bubbling of dry air into the electrolyte solution prior to the initial Li deposition was found to show an improved cycling number of the Li anode. On the other hand, the bubble introduction of pure gases of O_2, N_2 or CO_2, which are consisting of air, did lead to the lowering of the cycle number of the Li electrode compared to the electrode operated in Ar or dry air. From the results, it is clear that the SEI characteristic is very important to improve the efficiency of the metallic Li anodes. The atmosphere during the formation of metallic Li anodes, strongly influences the performance as anodes for Li batteries. The protective SEI layer against the side reaction occurring during the dissolution/deposition reaction of an anode would have a promising potential for the longer cycle life with a higher charge efficiency as the battery anode. The protective SEI layer is supposed to be formed at the initial deposition of Li and remained at the interface between the Li and electrolyte, as discussed in the literature [10,11].

Additionally, the protective property of the SEI layer formed on Li under the dry air was verified by the introduction of the ionic liquid (IL) additive of the electrolyte solution. 20 vol.% of ILs, such as BMP-TFSI, EMI-TFSI or DAI-TFSI were added to the electrolyte solution after the initial deposition of Li in the additive free electrolyte. As summarized in Table 2, the Li electrodeposited in the solution under the dry air atmosphere showed a small infection by the addition of ILs, while that deposited under Ar showed drastic decreases. Therefore, the SEI formed with dry air atmosphere, which consists of Li_2CO_3 and Li nitride, works well for the protective layer for cycling. While the SEI formed with Ar gas atmosphere, which consists of the Li_2CO_3 and Li_2O main-layer, does not work well. This leads to the conclusion that the Li_2CO_3 and Li nitride containing protective SEI work well for cycling and the IL additives do not effect it very much, while the IL additives affect for the Li deposited in Ar gas atmosphere whose SEI consists of Li_2CO_3. This difference in SEI may lead to the influence of the Li deposition reaction which results in the deposited morphology of Li. The protective SEI will proceed with a rather homogeneous deposition of Li during cathodic polarization compared with unprotecting SEI, as shown in Fig. 1.

From the discussions above, it is clear that the operation atmosphere for the anode materials of Li batteries has a very important role for the characteristics of the SEI layer formed on the anodes.

Table 1
Cycle numbers before reaching the potential to 1.0 V vs. Li/Li+ during the discharging of the Li anode in the constant current charge–discharge test. The initial Li was deposited and cycled in the electrolyte solution with the condition shown in table.

Atmosphere	Cycle number
Ar atmosphere	31
Dry air atmosphere	33
Dry air bubbled electrolyte	38
O_2 bubbled electrolyte	20
N_2 bubbled electrolyte	19
CO_2 bubbled electrolyte	23

Table 2
Cycle performance of Li anodes electrodeposited in the Ar atmosphere or the dry air atmosphere with the additive of ILs to the $1\,mol\,dm^{-3}$ $LiPF_6$/EC-DEC electrolyte.

Added IL	Cycle number (cycle efficiency/%)	
	Dry air	Ar atmosphere
0%	33 (88.9%)	31 (88.3%)
20% BMPTFSI	35 (89.5%)	21 (83.7%)
20% EMITFSI	32 (88.6%)	15 (78.5%)
20% DAITFSI	32 (88.6%)	13 (76.0%)

The atmosphere is strongly recommended to be mentioned in the research reports on Li batteries, and in order to improve the performance of the anodes, the atmosphere for the initial preparation of the anode/electrolyte interface should be considered.

4. Conclusion

The surface morphology and the SEI layer formed on the electrodeposited Li and the electrochemical activity of the Li anodes were characterized with the variation of atmosphere with dry Ar or dry air. The SEI formed on Li deposited in the dry air atmosphere, which consists of Li_2CO_3 and Li nitride, has proved to have more protective properties against the contaminants than that deposited in dry Ar atmosphere and leads to a rather flat surface of the deposited Li and higher deposition–dissolution efficiency.

Acknowledgements

References

[1] Y. Kobayashi, Y. Mita, S. Seki, Y. Ohno, H. Miyashiro, N. Terada, J. Electrochem. Soc. 154 (2007) A677–A681.
[2] H. Sakaebe, H. Matsumoto, K. Tatsumi, Electrochim. Acta 53 (2007) 1048–1054.
[3] K. Tsunashima, M. Sugiya, Electrochem. Solid-State Lett. 11 (2008) A17–A19.
[4] A. Watarai, K. Kubota, M. Yamagata, T. Goto, T. Nohira, R. Hagiwara, K. Ui, N. Kumagai, J. Power Sources 183 (2008) 724–729.
[5] K. Nishikawa, Y. Fukunaka, T. Sakka, Y.H. Ogata, J.R. Selman, Electrochim. Acta 53 (2007) 218–223.
[6] J.T. Vaughey, A.M. Geyer, N. Fackler, C.S. Johnson, K. Edstrom, H. Bryngelsson, R. Benedek, M.M. Thackeray, J. Power Sources 174 (2007) 1052–1056.
[7] K. Morigaki, A. Ohta, J. Power Sources 76 (1998) 159–166.
[8] Y.M. Lee, J.E. Seo, Y.-G. Lee, S.H. Lee, K.Y. Cho, J.-K. Park, Electrochem. Solid-State Lett. 10 (2007) A216–A219.
[9] D. Aurbach, B. Markovsky, A. Nimberger, E. Levi, Y. Gofer, J. Electrochem. Soc. 149 (2002) A152–A161.
[10] T. Osaka, T. Momma, K. Nishimura, T. Tajima, J. Electrochem. Soc. 140 (1993) 2745–2748.
[11] T. Osaka, T. Momma, Y. Matsumoto, Y. Uchida, J. Electrochem. Soc. 144 (1997) 1709–1713.
[12] N.S. Choi, Y.M. Lee, K.Y. Cho, D.H. Ko, J.K. Park, Electrochem. Commun. 6 (2004) 1238–1242.
[13] H. Ota, X.M. Wang, E. Yasukawa, J. Electrochem. Soc. 151 (2004) A427–A436.
[14] S.-T. Hong, J.-S. Kim, S.-J. Lim, W.Y. Yoon, Electrochim. Acta 50 (2004) 535–539.
[15] K. Kanamura, H. Tamura, Z. Takehara, J. Electroanal. Chem. 333 (1992) 127–142.
[16] D. Ahn, C. Kim, J.-G. Lee, B. Park, J. Solid State Chem. 181 (2008) 2139–2142.
[17] H. Wangh, W.-D. Zhang, Z.-Q. Deng, M.-C. Chen, Solid State Ionics 180 (2009) 212–215.
[18] V.R. Koch, J. Power Sources 6 (1981) 357–370.