Short communication

A study on lithium/air secondary batteries—Stability of the NASICON-type lithium ion conducting solid electrolyte in alkaline aqueous solutions

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ABSTRACT

The stability of the high lithium ion conducting glass ceramics, $Li_{1+x+y}Ti_{2-x}Al_xSi_yP_{3-y}O_{12}$ (LTAP) in alkaline aqueous solutions with and without LiCl has been examined. A significant conductivity decrease of the LTAP plate immersed in 0.057 M LiOH aqueous solution at 50 °C for 3 weeks was observed. However, no conductivity change of the LTAP plate immersed in LiCl saturated LiOH aqueous solutions at 50 °C for 3 weeks was observed. The pH value of the LiCl–LiOH–H$_2$O solution with saturated LiCl was in a range of 7–9. The molarity of LiOH and LiCl in the LiOH and LiCl saturated aqueous solution were estimated to be 5.12 and 11.57 M, respectively, by analysis of Li$^+$ and OH$^-$. The high concentration of LiOH and the low pH value of 8.14 in this solution suggested that the dissociation of LiOH into Li$^+$ and OH$^-$ is too low in the solution with a high concentration of Li$^+$. These results suggest that the water stable LTAP could be used as a protect layer of the lithium metal anode in the lithium/air cell with LiCl saturated aqueous solution as the electrolyte, because the content of OH$^-$ ions in the LiCl saturated aqueous solution does not increase via the cell reaction of $Li + 1/2O_2 + H_2O \rightarrow 2LiOH$, and LTAP is stable under a deep discharge state.

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1. Introduction

During the past few years, much attention has been paid to lithium/air secondary batteries, because they have the potential of the highest specific energy density of all galvanic cells. The theoretical energy density of the lithium/air batteries, excluding oxygen, is 11,140 Wh kg^{-1}, which is comparable to that of a gasoline/air. This battery system, therefore, is expected to develop a high specific energy density battery compared to internal engines used for vehicles, which is about 700 Wh kg^{-1} [1]. To develop an acceptable lithium/air battery for electric vehicles, a number of problems need to be resolved in relation to the electrolyte, the lithium anode, and the air electrode. Two types of the lithium/air secondary batteries have been developed, namely a non-aqueous electrolyte system and an aqueous electrolyte system. Bruce et al. reported attractive results for the cells with the non-aqueous electrolyte of LiPF$_4$ in propylene carbonate and a nano-carbon particle with a MnO$_2$ catalyst [2,3]. A high reversible cathode capacity more than 400 mAh g^{-1} (the cathode total mass) after 10 cycles was observed. This capacity is approximately three times higher than that of the cathode in a conventional lithium-ion battery. However, this system showed a high polarization, especially in the charging process. The high polarization causes decrease in the energy conversion efficiency. The energy losses in charging and discharging should be reduced for applications such as electric vehicles to save energy. To reduce the high polarization, a more active catalyst for the oxidation of Li$_2$O$_2$ or Li$_2$O (reaction product at the air electrode) should be developed, or a new electrolyte should be used.

In a previous paper, we have reported a water stable lithium metal electrode [4]. This lithium electrode consists of a lithium metal, a polymer electrolyte, and a water stable lithium conducting glass ceramics, $Li_{1+x+y}Ti_{2-x}Al_xP_{3-y}Si_yO_{12}$ (LTAP). The use of this glass ceramics was proposed in 2004 as a protect layer for the lithium metal electrode by Visco et al. [5]. We have used a polymer electrolyte as a buffer layer to protect the reaction of lithium metal and the glass ceramics, because the LTAP is unstable in direct contact with lithium metal. This type of water stable lithium metal electrode could be used potentially for the lithium/air secondary batteries as the anode. The charge and discharge polarization of the Li/polymer electrolyte/LTAP/1 M LiCl/Pt, air cell at 1.0 mA cm^{-2} and 60 °C was as low as 0.24 and 0.25 V, respectively [4]. The cell

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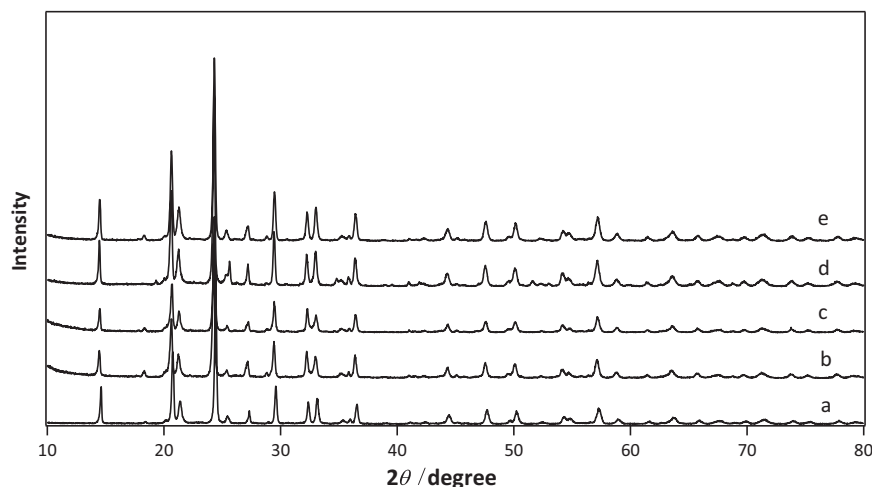*E-mail address:* imanishi@chem.mie-u.ac.jp (N. Imanishi).

Fig. 1. XRD profiles of (a) the pristine LTAP plate, (b) the LTAP plate immersed in 0.057 M LiOH aqueous solution at 50 °C for 3 weeks, (c) the LTAP plate immersed in 0.57 M LiOH aqueous solution at 50 °C for 3 weeks, (d) the LTAP plated immersed in saturated LiOH aqueous solution at 50 °C for 3 weeks, and (e) the LTAP plate immersed in 11.6 M LiCl–5.1 M LiOH–H$_2$O at 50 °C for 3 weeks.

reaction of the lithium/air battery with an aqueous electrolyte is as follows:

$$2Li + 1/2O_2 + H_2O = 2LiOH \qquad (1)$$

The energy density of this system is calculated to be 6365 Wh kg^{-1} by weights of Li and H$_2$O and an open circuit voltage (OCV) of 3.8 V. The calculated energy density is lower than that of the non-aqueous lithium/air batteries, because water is active material, although the calculated energy density is still high compared to the other battery system as Li/sulfur (about 2500 Wh kg^{-1}). However, we have observed that the LTAP was unstable in strong basic and acidic solution [6]. According to Eq. (1), the OH$^-$ concentration increases with increasing discharge depth, which results in the decomposition of LTAP. We have proposed a new type of lithium/air secondary battery with an acetic acid solution to prevent the increase of the OH$^-$ concentration in the deep discharge [7], where the cell reaction is as follows:

$$2Li + 1/2O_2 + 2CH_3COOH = 2CH_3COOLi + H_2O \qquad (2)$$

The energy density of this system was calculated to be 1478 Wh kg^{-1}, which is only about 20% of that of the aqueous lithium/air cell. In this study, we examined the stability of LTAP in LiCl–LiOH–H$_2$O and found that LTAP is stable in a high concentration of LiCl aqueous solutions with saturated LiOH. These results suggest that we have the possibility to develop a high energy density lithium/air secondary battery with low charge and discharge polarizations using an aqueous solution

2. Experimental

The water stable NASICON-type lithium conducting glass ceramic (LTAP), Li$_{1+x+y}$Ti$_{2-x}$Al$_x$Si$_y$P$_{3-y}$O$_{12}$ ($x \approx 0.25$ and $y \approx 0.1$), plates were supplied by OHARA Inc., Japan. The preparation method of LTAP has been described in the literature [8]. The thickness of the LTAP plate was about 0.25 mm and the electrical conductivity at room temperature is 3.3×10^{-4} S cm^{-1}.

The stability tests of LTAP in aqueous solutions were carried out for the sintered glass ceramics LTAP plates. The LTAP plates were immersed in aqueous solutions with various concentrations of LiCl and LiOH at 50 °C for 3 weeks. The samples immersed in the aqueous solutions were washed with water and dried at 220 °C for overnight to remove the water. The changes of XRD patterns, the surface morphology, and the electrical conductivity before and after immersion in the LiCl–LiOH–H$_2$O solutions were examined.

XRD data were obtained using a Rigaku RINT 2500 with rotating copper cathode. Scanning electron microscope (SEM) images were measured using a Hitachi SEM S-4800. The content of Li$^+$ in the aqueous solutions was determined using a Shimadzu inductively coupled plasma spectrometer (ICP) and the content of Cl$^-$ ions using a chloride meter CL-5Z, KRK, Japan.

The electrical conductivity of the LTAP plates with sputtered gold electrodes was measured using a Solartron 1260 frequency response analyzer in the frequency range 0.1 Hz to 1 MHz and the temperature range 25–80 °C. Z plot software was employed for data analysis.

3. Results and discussion

According to our previous results [6], LTAP is unstable in LiOH aqueous solution. The LTAP immersed in the 1 M LiOH aqueous solution at 50 °C for 3 weeks showed trace extra peaks in XRD patterns and the significant surface morphology change. In this study, the effect of LiOH concentration on the stability of LTAP was examined. Fig. 1 shows the XRD results of the LTAP plate immersed in LiCl–LiOH–H$_2$O solutions at 50 °C for 3 weeks. The pristine LTAP shows the diffraction profile indexed by the NASICON-type structure [8] with some extra diffraction peaks of AlPO$_4$ ($2\theta \approx 21.2$) and TiO$_2$ ($2\theta \approx 27.4$). These extra diffraction peaks were not found in the LTAP plate used in the previous study [6]. The LTAP plates immersed in 0.57 and 0.057 M LiOH aqueous solutions show the same diffraction profiles to that of the pristine LTAP and that immersed in saturated LiOH aqueous solution shows trace unknown extra diffraction peaks. An exciting result was found for the LTAP plate immersed in the saturated LiCl and LiOH aqueous solution at 50 °C for 3 weeks. There were no signs of any change to the XRD patterns before and after immersion in this solution, which was prepared by addition of excess LiOH into the LiCl saturated aqueous solution and by filtering the precipitates. The solubility limit of LiOH in water is about 5 M at room temperature. It is quite strange that the pH value of the saturated LiCl and LiOH aqueous solution was as low as 8.14, which is compared to 12.90 for 0.57 M LiOH aqueous solution.

Generally, the solubility of a salt in water decreases by addition of the other salt [9]. Fig. 2 shows the experimental solubility of LiOH as a function of the concentration of LiCl in LiOH–LiCl–H$_2$O at room temperature along with the pH values. The excess LiOH salt was added into different concentration of LiCl aqueous solutions and the solutions were kept stirred overnight at room temperature, and then filtered. The filtrate was used to analyze the content of Li$^+$ and
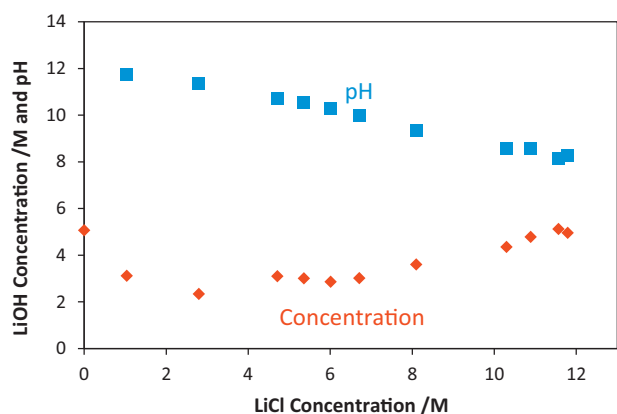
Fig. 2. LiOH solubility and pH of the LiOH–LiCl–H$_2$O system at room temperature.

Cl$^-$, and pH values. The concentration of LiOH was estimated from the difference of the mole fraction of Li$^+$ and Cl$^-$. The solubility of LiOH decreases with increasing content of LiCl in LiCl–LiOH–H$_2$O to about 2 M, and then turns into increase. The solubility limit of LiOH in water and the saturated LiCl aqueous solution at 25 °C are 5.06 and 5.12 M, respectively. It is not clear why the LiCl–LiOH–H$_2$O system shows such a solubility behavior. Intermediate compounds of LiCl·LiOH and 2LiCl·3LiOH have been reported in the LiCl–LiOH system [10]. The solubility of these compounds in water may play a role, but we need more detailed studies on the solubility of the LiOH–LiCl–H$_2$O system.

The pH values of the LiOH–LiCl–H$_2$O system are quite interesting. The pH of 0.00057 M LiOH and 0.0057 M LiOH were 10.91 and 11.91, respectively. The pH values of the system do not depend on the concentration of LiOH, but monotonously decrease with increasing content of LiCl. The pH values of 11.6 M LiCl–5.1 M LiOH–H$_2$O and 1.04 M LiCl–3.1 M LiOH–H$_2$O were 8.14 and 11.7, respectively. These results suggest that excess amount of Li$^+$ ions

in LiOH–LiCl–H$_2$O restrains the dissociation of LiOH to Li$^+$ and OH$^-$. This is an interesting result for the lithium/air secondary battery with an aqueous electrolyte using a LTAP protected lithium metal anode. The LiCl saturated aqueous solution gives a slight increase in pH from 7.0 to 8.14 with increasing LiOH content by the discharge process. Therefore, the water stable lithium metal electrode with LTAP is stable at a deep discharge state, where the electrolyte solution is saturated with LiOH.

The stability of the LTAP plate immersed in LiOH–LiCl–H$_2$O was also confirmed from SEM observations. Fig. 3 shows the SEM images of the LTAP plates immersed in the 0.57 M LiOH aqueous solution, the 0.1 M HCl aqueous solution, and the 11.6 M LiCl and 5.1 M LiOH aqueous solution at 50 °C for 3 weeks. Significant surface morphology changes are observed in the LTAP immersed in the 0.57 M LiOH aqueous solution and in the 0.1 M HCl aqueous solution. These morphology changes may be due to the reaction of LTAP with acid and alkaline solutions. While, 11.6 M LiCl and 5.1 M LiOH aqueous solution shows no surface morphology change.

In a previous paper [6], we observed that the electrical conductivity of the LTAP plates decreased extremely by immersion in a 1 M LiOH aqueous solution for 8 months at room temperature. The conductivity stability of LTAP in the LiOH saturated aqueous solution is a key factor for a long-term use of the lithium/air batteries as a power source for electric vehicles. According to Eq. (1), the calculated concentration of LiOH in the 50% discharge depth is about 100 M. Therefore, almost all the LiOH is precipitated in the electrolyte solution, because the solubility limit of LiOH in water is only about 5 M. The solution reaches the saturation at a few % of discharge depth. The impedance spectra of the LTAP plates immersed in aqueous solutions with different concentrations of LiOH at 50 °C for 3 weeks are shown in Fig. 4. The spectrum of the LTAP immersed in a low content of 0.00057 M LiOH aqueous solution (pH 10.91) shows a semicircle, which could be attributed to a grain boundary resistance of LTAP. The intercept of the semicircle on the real axis at high frequency represents the bulk resistance. The linear Warburg element following the semicircle may be attributed to specimen
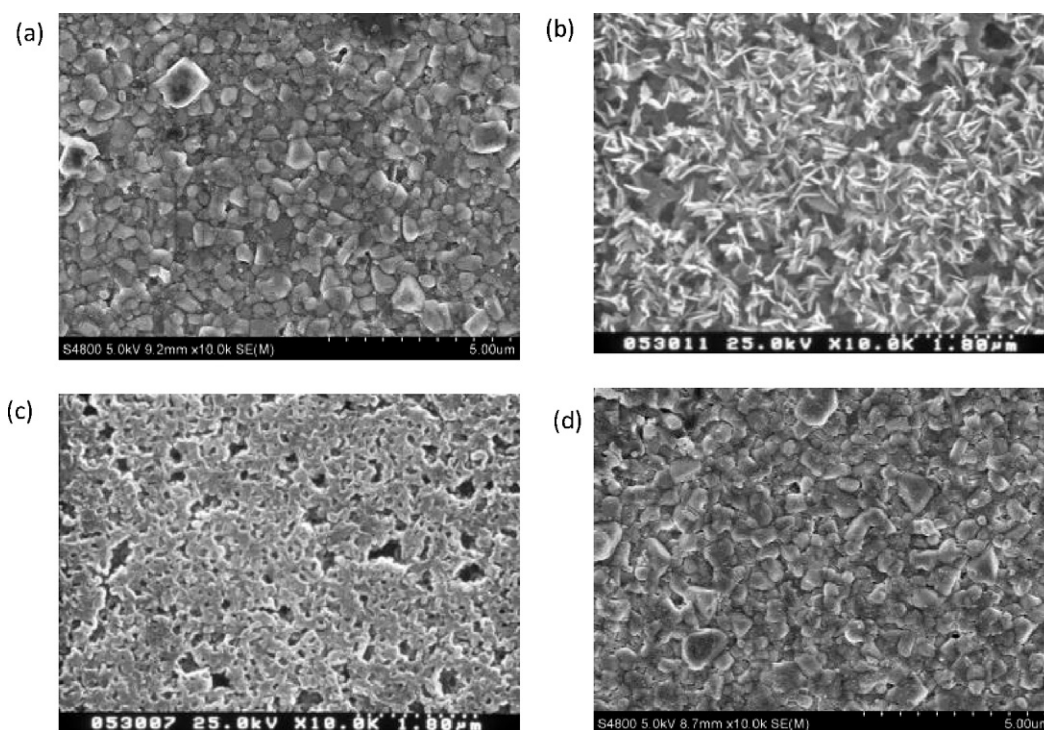

Fig. 3. SEM images of (a) the pristine LTAP plate, (b) the LTAP plate immersed in the 0.57 M LiOH aqueous solution at 50 °C for 3 weeks, (c) the LTAP plate immersed in the 0.1 M HCl aqueous solution at 50 °C for 3 weeks, (d) the LTAP plate immersed in 11.6 M LiCl and 5.1 LiOH aqueous solution at 50 °C for 3 weeks.
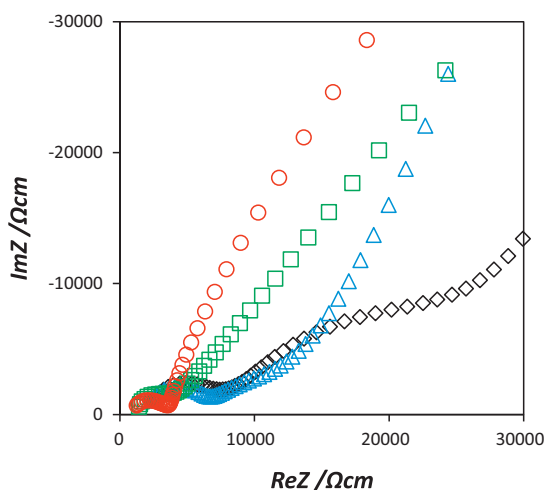
Fig. 4. Impedance profiles at 25 °C of the LTAP plates immersed in (○) 0.57 M LiOH, (△) 0.057 M LiOH, (◇) 0.0057 M LiOH, and (□) 0.00057 M LiOH at 50 °C for 3 weeks.

Fig. 5. Impedance profiles at 25 °C of (○) the pristine LTAP plate, and the LTAP plates immersed in 11.6 M LiCl–5.1 M LiOH–H_2O and (△) the LTAP plate immersed in the saturated $LiNO_3$–3 M LiOH–H_2O at 50 °C for 3 weeks.

interaction observed for a typical ion conducting solid electrolyte with a blocking electrode [11]. The bulk and the grain boundary specific resistances of the LTAP plate immersed in 0.00057 M LiOH aqueous solution at 50 °C for 3 weeks were estimated to be 869 and 2712 Ω cm at 25 °C, respectively. These resistances correspond to 1.1×10^{-3} and 3.7×10^{-4} S cm^{-1}, respectively. The total conductivity of 1.9×10^{-4} S cm^{-1} is slightly lower than that of the pristine plate (3.46×10^{-4} S cm^{-1}). The impedance spectrum of the LTAP plate immersed in 0.0057 M solution shows similar profile to that of immersed in 0.00057 M LiOH solution. The LTAP plate immersed in a concentrated LiOH solution shows a significant increase in the resistance, especially, in the grain boundary resistance. The impedance spectrum of the LTAP immersed in the 0.57 M LiOH aqueous solution shows a second deformed large semicircle. This semicircle is possibly attributed to the resistance of decomposition product segregated in the grain boundary region. The bulk and the grain boundary conductivities at 25 °C were 6.6×10^{-4} and 2.8×10^{-5} S cm^{-1}, respectively. While the bulk conductivity degradation is not significant, the grain boundary conductivity shows about one order lower value than pristine LTAP (5.1×10^{-4} S cm^{-1}). The conductivity of LTAP immersed in 1 M LiOH aqueous solution for 8 months decreased to 5.2×10^{-7} S cm^{-1} at room temperature [6].

In Fig. 5, the impedance profile at 25 °C of the pristine LTAP plate is compared with the LTAP plate immersed in LiCl and LiOH saturated aqueous solution (11.6 M LiCl and 5.1 M LiOH) at 50 °C for 3 weeks. The impedance profile of the LTAP immersed in the aqueous solution (pH 8.14) shows no significant change and only the grain boundary resistance slightly increases. No bulk conductivity change is observed and the grain boundary conductivity decreases from 5.1×10^{-4} to 2.7×10^{-4} S cm^{-1}. The impedance profile of the LTAP immersed in the solution shows no second deformed semicircle which appears in the LTAP immersed in a high concentration LiOH solution. A similar result is observed in the LTAP immersed in $LiNO_3$–LiOH–H_2O solution. The impedance profile of the LTAP plate immersed in saturated $LiNO_3$–3 M LiOH–H_2O (pH 9.79) at 50 °C for 3 weeks is also shown in Fig. 5. This is a similar impedance profile to that of the LTAP immersed in saturated LiCl–LiOH–H_2O. These results clearly show that the stability of LTAP depends on the pH value of the solution.

The conductivity of the LTAP slightly decreased after immersion in the saturated LiCl and LiOH aqueous solution for 3 weeks. Longer-term stability of LTAP in the same solution was carried out and the impedance profiles of the LTAP plates immersed in the solution for
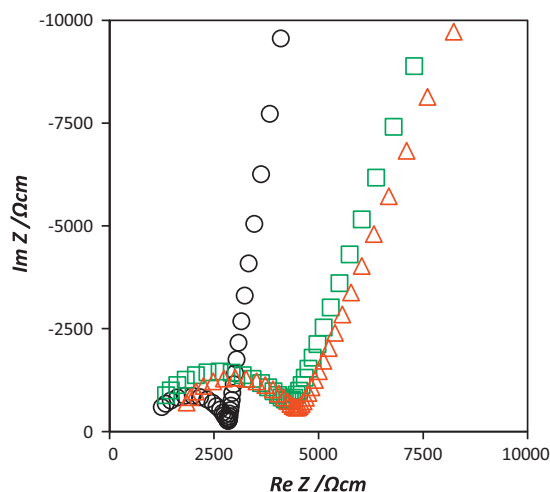
3 months and for 3 weeks at 50 °C were compared. As shown in Fig. 6, no significant change of the impedance profile is observed in the period examined. The bulk conductivity of 1.2×10^{-3} S cm^{-1} shows no change for the LTAP immersed for 3 months at 50 °C and the grain boundary conductivity slightly increases from 2.7×10^{-4} to 3.3×10^{-4} S cm^{-1}. We could conclude that LTAP is stable in the saturated LiCl and LiOH aqueous solution.

The temperature dependences of the total conductivity, the bulk conductivity, and the grain boundary conductivity of the LTAP immersed in 11.6 M LiCl–5.1 M LiOH–H_2O solution at 50 °C for 3 weeks are shown in Fig. 7, where these conductivities were estimated from the impedance profiles using a simple series combination of the bulk resistance and the grain boundary resistance with a capacitance. The activation energy for the bulk and the grain boundary conductivities were estimated from the temperature dependence to be 4.1 and 47.5 kJ mol^{-1}, respectively. They are slightly lower than energies of 6.8 and 59.1 kJ mol^{-1} for the pristine LTAP [12]. These differences may be within experimental errors.

As shown in Fig. 2, the LiOH–LiCl–H_2O solution with high content of LiCl shows low pH values. The conductivity study suggests that the stability of the LTAP plate in the LiCl–LiOH–H_2O solution may depend on the pH value of the solution. In Table 1, the conduc-
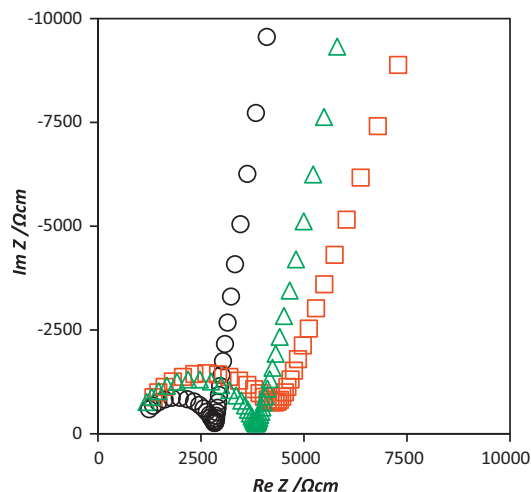

Fig. 6. Impedance profiles at 25 °C of the LTAP plate immersed in (□) 11.6 M LiCl–5.1 M LiOH–H_2O at 50 °C for 3 weeks, (△) 3 months, and (○) the pristine LTAP.
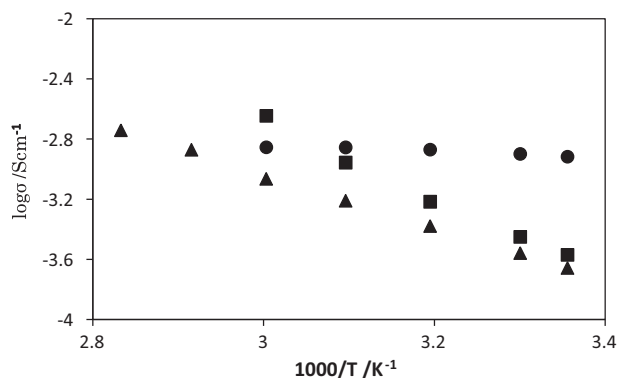
Fig. 7. Arrhenius plots of bulk conductivity (●), grain boundary conductivity (■), and total conductivity (▲) for the LTAP plate immersed in 11.6 M LiCl–5.1 M LiOH–H$_2$O at 50 °C for 3 weeks.

Table 1

Electrical conductivity of the LTAP plate immersed in LiCl–LiOH–H$_2$O at 50 °C for 3 weeks.

LiOH concentration (M)	LiCl concentration (M)	pH	Conductivity at 25 °C (S cm^{-1})
0.57	0	12.90	0.27×10^{-4}
0.057	0	12.78	0.58×10^{-4}
0.0057	0	11.91	1.7×10^{-4}
0.00057	0	10.91	2.0×10^{-4}
3.6	8.10	9.36	2.51×10^{-4}
5.0	11.8	8.25	2.61×10^{-4}
5.1	11.6	8.14	2.32×10^{-4}
2.3	10.4	7.62	2.55×10^{-4}
0.18	12.6	7.01	3.11×10^{-4}

tivities at 25 °C of the LTAP plates immersed in the LiOH–LiCl–H$_2$O solutions at 50 °C for 3 weeks are summarized in order of the pH values of the solutions. As shown in this table, the pH value of LiCl–LiOH–H$_2$O is not high, that is, the dissociation of LiOH to Li$^+$ and OH$^-$ is suppressed by the high concentration of Li$^+$ according to the mass action law. These results clearly suggest that the stability of the LTAP plate in the aqueous solution depends on the pH value of the solution, and the LTAP plate is stable in the pH range less than 10. The stability of the LTAP in the saturated LiNO$_3$–LiOH

aqueous solution could also be explained from the low pH value of 9.79.

4. Conclusions

The lithium ion conducting glass ceramics of Li$_{1+x+y}$Ti$_{2-x}$Al$_x$Si$_y$P$_{3-y}$O$_{12}$ was found to be unstable in alkaline solution of pH 10 or more. By immersing the LTAP plate in such alkaline solution, the high resistance phase was segregated at the grain boundary in LTAP, and the electrical conductivity decreased significantly. On the other hand, the LTAP plate was stable in saturated LiCl and LiOH solution, because the pH value of the solution is less than 10. The low pH value could be explained by the low dissociation of LiOH to ions in the existence of high concentration of Li$^+$ ions. We could conclude that the LTAP plate could be used as a protect layer for the water stable lithium metal electrode in the lithium/air batteries with saturated LiCl aqueous solution, because the reaction product of LiOH does not dissociate to ions in the LiCl saturated aqueous solution. The LTAP plate is stable even in the deep discharge state. This type of lithium/air system could be expected to develop as a high specific energy density secondary battery comparable to an internal combustion engine.

References

[1] M. Armand, J.-M. Tarascon, Nature 451 (2008) 652.
[2] A. Ogasaware, A. Debart, M. Holtzapefel, P. Novak, P.J. Bruce, J. Am. Chem. Soc. 129 (2006) 1390.
[3] A. Debart, A.J. Paterson, J. Bao, P.G. Bruce (Eds.), Angew. Chem. Int. 47 (2008) 4521.
[4] T. Zhang, N. Imanishi, S. Hasegawa, A. Hirano, J. Xie, Y. Takeda, O. Yamamoto, N. Sammes, Electrochem. Solid-State Lett. 12 (2009) A132.
[5] S.J. Visco, E. Nomon, B. Katz, L.C.D. Jongle, M.Y. Chu, Abstract #53, The 12th International Meeting on Lithium Batteries, Nara, Japan, 2004.
[6] S. Hasegawa, N. Imanishi, T. Zhang, J. Xie, A. Hirano, Y. Takeda, O. Yamamoto, J. Power Sources 189 (2009) 371.
[7] T. Zhang, N. Imanishi, Y. Shimonishi, A. Hirano, Y. Takeda, O. Yamamoto, Chem. Commun. 46 (2010) 1661.
[8] J. Fu, Solid State Ionics 96 (1997) 195.
[9] A. Jaretin, G. Aly, Fluid Phase Equilib. 175 (2000) 213.
[10] N.A. Reshetnikov, G.M. Unzhakov, Zhur, Neorg. Khim. 3 (1958) 1435.
[11] P.G. Bruce, A.R. West, J. Electrochem. Soc. 130 (1983) 652.
[12] T. Zhang, N. Imanishi, S. Hasegawa, A. Hirano, J. Xie, Y. Takeda, O. Yamamoto, N. Sammes, J. Electrochem. Soc. 155 (2008) A965.