Journal of Power Sources 195 (2010) 6187–6191

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

A study on lithium/air secondary batteries—Stability of NASICON-type glass ceramics in acid solutions

Y. Shimonishi[a], T. Zhang[a], P. Johnson[b], N. Imanishi[a,*], A. Hirano[a], Y. Takeda[a], O. Yamamoto[a], N. Sammes[b]

[a] *Department of Chemistry, Faculty of Engineering, Mie University, 1577 Kurimamachiay-cho, Tsu, Mie 514-8507, Japan*
[b] *Department of Metallurgical and Materials Engineering, Colorado School of Mines, 1500 Illinois Street, Golden, CO 80401, USA*

ARTICLE INFO

Article history:
Received 20 September 2009
Received in revised form 4 November 2009
Accepted 4 November 2009
Available online 13 November 2009

Keywords:
Metal air battery
NASICON
Glass ceramics
Acetic acid

ABSTRACT

The stability of a NASICON-type lithium ion conducting solid electrolyte, $Li_{1+x+y}Ti_{2-x}Al_xP_{3-y}Si_yO_{12}$ (LTAP), in acetic acid and formic acid solutions was examined. XRD patterns of the LTAP powders immersed in 100% acetic acid and formic acid at 50 °C for 4 months showed no change as compared to the pristine LTAP. However, the electrical conductivity of LTAP drastically decreased. On the other hand, no significant electrical conductivity change of LTAP immersed in lithium formate saturated formic acid–water solution was observed, and the electrical conductivity of LTAP immersed in lithium acetate saturated acetic acid–water increased. Cyclic voltammogram tests suggested that acetic acid was stable up to a high potential, but formic acid decomposed under the decomposition potential of water. The acetic acid solution was considered to be a candidate for the active material in the air electrode of lithium–air rechargeable batteries. The cell reaction was considered as $2Li + 2\,CH_3COOH + 1/2O_2 = 2CH_3COOLi + H_2O$. The energy density of this lithium–air system is calculated to be 1477 Wh kg^{-1} from the weights of Li and CH_3COOH, and an observed open-circuit voltage of 3.69 V.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

To improve the energy conversion efficiency for vehicles and to reduce the production of CO_2, electric vehicles (EV) have been considered as the best candidates for many years. However, only a few EVs for general use have been demonstrated, because acceptable batteries have not yet been developed. The most important item for the EV battery is to improve the energy density. At present, the energy density of the battery is less than 200 Wh kg^{-1} [1]. The energy density is far from that of the internal combustion engine, so the driving range of the EV is too short compared to vehicles with a conventional internal combustion engine. We need to develop a battery with an energy density as high as 700 Wh kg^{-1} to be comparable to the conventional internal combustion engine. This energy density is the final target of the New Energy and Industrial Technology Development Organization (NEDO), Japan, project for batteries in next-generation vehicles. Such a high energy density battery could be achieved only in a few electrochemical systems. Of these, the lithium–air battery is the most attractive, because it has the highest energy density of all galvanic cells. The first challenge for the rechargeable lithium–air battery was reported by Abraham and Jiang in 1996 [2]. They were studying the reversible reaction in the cell with a gel-type polymer electrolyte and a carbon electrode with cobalt phthalocyanine as the catalyst. A reversible capacity of 630 mAh per gram of carbon was observed. Recently, Bruce et al. reported an attractive result for a cell with a non-aqueous electrolyte and a nano carbon particle with a MnO_2 catalyst. A high reversible capacity of 600 mAh per gram of carbon was achieved after 50 cycles [3]. These attractive results were obtained under pure oxygen. However, the active life is limited by the diffusion of water and oxygen from air through the electrolyte to the lithium metal anode. The electrochemical performance of the lithium–air cell was drastically reduced when the cell was cycled in air even though a hydrophobic membrane was used to prevent the moisture in the air [4]. Thus, protection of the lithium metal anode from water is the most critical point for the long life stability of the lithium–air batteries as pointed out by Armand and Tarascon [1].

In our previous paper [5,6], we proposed a water-stable lithium metal anode which was covered by a water-stable lithium conducting solid electrolyte, $Li_{1.35}Ti_{1.75}Al_{0.25}Si_{0.1}P_{0.9}O_{12}$ (LTAP), and found that a Li/polymer electrolyte/LTAP/aqueous LiCl/Pt, air cell showed excellent electrochemical performance. However, we observed that the water-stable solid electrolyte is unstable in strong basic and acidic solutions [7]. XRD patterns of the LTAP immersed in 1 M aqueous LiOH solution for 3 weeks at room temperature showed a decomposition product of Li_3PO_4, and the electrical conductivity drastically decreased. The cell reaction of the lithium–air battery

---

* Corresponding author. Tel.: +81 59 231 9420; fax: +81 59 231 9478.
E-mail address: imanishi@chem.mie-u.ac.jp (N. Imanishi).

0378-7753/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2009.11.023

with aqueous electrolyte solution is as follows:

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

OH^- ions are produced by the discharging process, and the concentration of OH^- in the solution increases with the discharge depth. This type of water-stable lithium electrode, therefore, is not acceptable for the system with the cell reaction (1). We need to search for a new lithium–air system. Weak acids such as acetic acid (HAc) and formic acid (HFc), are the candidates for this new system. The cell reaction of the system with acetic acid is,

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

where the reaction products are lithium acetate (LiAc) and water, and the pH in the solution is relatively constant.

In this study, the stability of LTAP in the acetic acid and formic acid solutions has been examined and the possibility of a lithium–air system with a weak acid solution has been discussed.

2. Experimental

The water-stable NASICON-type lithium conducting solid electrolyte, $Li_{1+x+y}Ti_{2-x}Al_xSi_yP_{3-y}O_{12}$ (LTAP) powder and plates were supplied by OHARA Inc., Japan. The preparation method of LTAP has been described in the literature [8].

The composite lithium anode was made by stacking three layers of lithium sheet, polymer electrolyte sheet, and LTAP plate. The polymer electrolyte used was polyethylene oxide (Mv = 600,000) doped with lithium bis(trifluoromethane sulfone)imide (LiTFSI) to make a composition Li/O = 1/18. The thickness of the sheet was about 200 μm. It was dried under vacuum at 110 °C for 12 h before set in the anode.

X-ray diffraction (XRD) data were obtained using a Rigaku RINT 2500 with a rotating copper cathode. Scanning electron microscope (SEM) images were measured using a Hitachi SEM S-4000.

The stability tests in the solution were carried out for the sintered LTAP tablet and powder. The LTAP powder (particle size of 1–10 μm) and the sintered LTAP tablet (about 0.2 cm in thickness) were immersed in an acid solution at 50 °C for at least 3 weeks. The sintered tablets were prepared by isostatically pressing the LTAP powder at 150 MPa and annealing in a temperature range 800–1000 °C for 12 h at air. The XRD patterns of the samples were compared before and after immersion in the solution. The electrical conductivity of the sintered LTAP tablets with sputtered gold electrodes was measured using a Solatron 1260 frequency response analyzer in the frequency range 0.01 Hz–1 MHz. *Z* plot software was employed for data analysis. The ac conductivities of the CH_3COOH (HAc)–H_2O–saturated CH_3COOLi (LiAc) and HCOOH (HFc)–H_2O–saturated LiCOOH (LiFc) solutions were measured as a function of the H_2O content in the solution using platinum with platinum black electrodes at room temperature. The contents of the lithium ion in HAc–H_2O–saturated LiAc and HFc–H_2O–saturated LiFc solutions were determined using a Shimazu ICPS 1000. The cyclic voltammograms were measured using a Hokuto HSV 100 automatic polarization system under atmosphere. A platinum electrode with platinum black was used as the working and counter electrodes.

3. Results and discussion

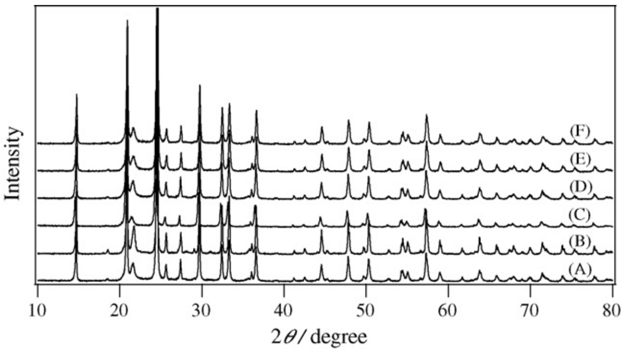

Fig. 1. XRD patterns of the LTAP powders immersed in HAc–H_2O–LiAc at 50 °C for 3 weeks. (A) Pristine LTAP, (B) immersed in HAc, (C) immersed in HAc (95 v/o)–H_2O (5 v/o)–LiAc (saturated), (D) immersed in HAc (90 v/o)–H_2O (10 v/o)–LiAc (saturated), (E) immersed in HAc (85 v/o)–H_2O (15 v/o)–LiAc (saturated), and (F) immersed in HAc (80 v/o)–H_2O (20 v/o)–LiAc (saturated).

According to our previous study [7], LTAP is unstable in strong acids. The LTAP immersed in 0.1 M HCl aqueous solution for 3 weeks at room temperature showed no extra XRD peak, but a conductivity decrease of about one order of magnitude was observed. The sample immersed in aqueous 5 M HCl solution for 1 week at 50 °C shows a completely different XRD pattern. Fig. 1 shows the XRD results of LTAP immersed in the HAc–H_2O–saturated LiAc solutions with various concentrations of HAc for 3 weeks at 50 °C. As shown in this figure, no changes in the XRD patterns were observed. The XRD patterns of the LTAP powder immersed in the HFc–H_2O–saturated LiFc solution are shown in Fig. 2. The pH of HFc (90 v/o)–H_2O (10 v/o)–LiFc (saturated) was 1.76, which is slightly lower than that of HAc (90 v/o)–H_2O (10 v/o)–LiAc (saturated), 3.34. No significant change of the XRD patterns was observed for the LTAP powders immersed in HFc–H_2O–LiFc for 3 weeks at 50 °C. Thus, XRD data confirms that the LTAP powder is very stable in the HAc–H_2O–LiAc and HFc–H_2O–LiFc solutions.

The LTAP glass ceramics was prepared by crystallizing the NASICON phase in the glass matrix. It has a structure that crystalline LTAP particles form a main part and a glass component fills the interspaces. The glass region at the grain boundary can realize fast ionic transfer between grains. The electrical conductivity of the glass ceramics was observed to be as high as $1 \times 10^{-3}\,S\,cm^{-1}$ at room temperature in the samples quenched from the melt phase and crystallized at 950 °C [8]. The sintered samples from the glass ceramic powder showed a high grain boundary resistance [5]. According to the XRD study, LTAP was stable in the weak acid solutions such as acetic acid and formic acid. However, the change of the glassy phase in LTAP cannot be detected by the XRD study. The impedance spectra are useful in detecting the change in the grain boundary resistance in the sintered LTAP tablets. As reported in previous papers [7,9], the grain boundary resistance dominated in the sintered LTAP plate and the electrical conductivity decrease of LTAP immersed in pure water diminished by the addition of

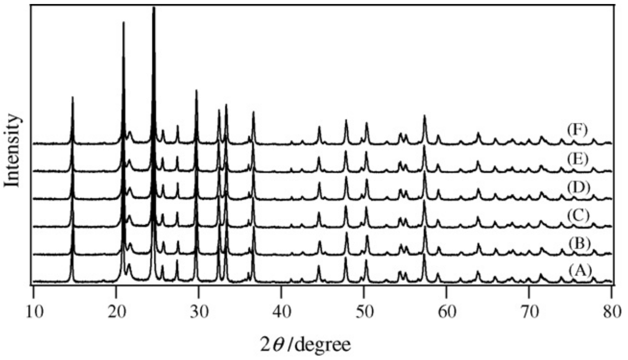

Fig. 2. XRD patterns of the LTAP powders immersed in HFc–H_2O–LiFc at 50 °C for 3 weeks. (A) Pristine LTAP, (B) immersed in HFc, (C) immersed in HFc (95 v/o)–H_2O (5 v/o)–LiFc (saturated), (D) immersed in HFc (90 v/o)–H_2O (10 v/o)–LiFc (saturated), (E) immersed in HFc (85 v/o)–H_2O (15 v/o)–LiFc (saturated), and (F) immersed in HFc (80 v/o)–H_2O (20 v/o)–LiFc (saturated).

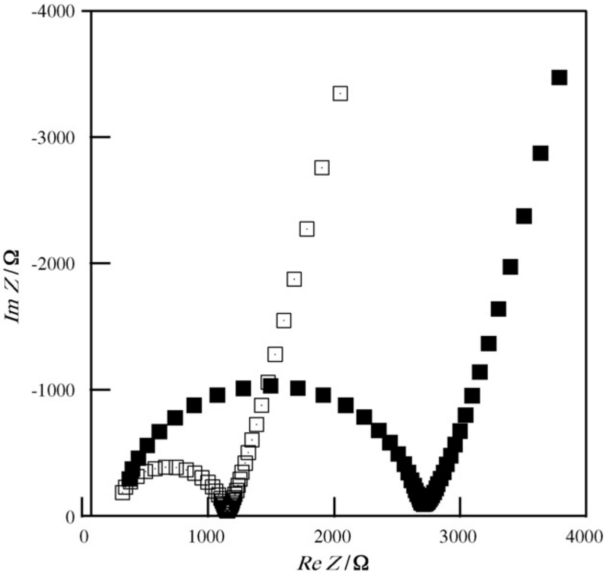

Fig. 3. Typical impedance spectra at room temperature of the pristine sintered LTAP tablet (■) and the sintered LTAP tablet immersed in HAc (90 v/o)–H_2O (10 v/o)–LiAc (saturated) (□) at 50 °C for 3 weeks.

$LiNO_3$ in the water. The electrical conductivity of the LTAP plate immersed in pure HAc for 4 months at 50 °C drastically decreased from 1.6×10^{-4} S cm^{-1} to 4.8×10^{-7} S cm^{-1} at room temperature. The LTAP powder immersed in 100% HAc and HFc solutions for 4 months at 50 °C also showed no significant change in the XRD patterns, but a few extra trace peaks were observed. The low conductivity of the LTAP immersed in HAc could be explained by the high grain boundary resistance observed in the impedance spectra. The impedance profiles of the LTAP tablet immersed in HAc (90 v/o)–H_2O (10 v/o)–LiAc (saturated) for 3 weeks at 50 °C are shown in Fig. 3, along with that of the pristine LTAP. The pressed LTAP tablets were sintered at 1000 °C for 12 h and the XRD patterns of the sintered tablet were exactly the same as that of the pristine LTAP powder shown in Fig. 1. The impedance spectrum of the pristine LTAP shows a semicircle and the semicircle decreased by immersing the LTAP in the acetic acid solution. The semicircle is attributed to the grain boundary resistance of the LTAP. The intercept of the semicircle on the real axis at high frequency represents the bulk resistance of the LTAP [10]. The bulk resistance and the grain boundary resistance of the pristine LTAP were estimated to be 290 Ω cm^2 and 1460 Ω cm^2. These resistances correspond to 9.2×10^{-4} S cm^{-1} and 1.8×10^{-4} S cm^{-1}, respectively, and the total electrical conductivity of 1.5×10^{-4} S cm^{-1} is comparable to those reported previously for $Li_{1.3}Ti_{1.7}Al_{0.3}P_3O_{12}$ prepared by a solid state reaction [11] and a sol–gel method [12]. The LTAP immersed in HAc (90 v/o)–H_2O (10 v/o)–LiAc (saturated) shows a small semicircle, and the bulk resistance and the grain boundary resistance were estimated to be 153 Ω cm^2 and 417 Ω cm^2, respectively. The grain boundary resistance was reduced a lot, while the bulk resistance was reduced only slightly, compared to the pristine LTAP. The total conductivity is as high as 4.7×10^{-4} S cm^{-1} at 25 °C. The enhancement of the electrical conductivity by immersing LTAP in the acetic acid solution could be explained by reducing the grain boundary resistance. This means that a high resistance grain boundary phase may be removed by immersing in the acetic acid solution, but the details are not yet clear. We can conclude that LTAP is stable in HAc (90 v/o)–H_2O (10 v/o)–LiAc (saturated). The electrical conductivity of the sintered samples is dependent upon the sintered temperature. The maximum conductivity was found for the sample sintered at 1000 °C for 12 h. The LTAP sintered at 1100 °C showed very low conductivity and a second phase was observed in the XRD patterns. The electrical conductivity of the LTAP tablet immersed in HFc (90 v/o)–H_2O (10 v/o)–LiFc (saturated) for 3 weeks at 50 °C showed no significant change compared to that of the pristine LTAP tablet. Table 1 shows the electrical conductivity data for the LTAP tablets sintered at various temperatures for 12 h before and after immersion in HAc (90 v/o)–H_2O (10 v/o)–LiAc (saturated) and HFc (90 v/o)–H_2O (10 v/o)–LiFc (saturated). All samples immersed in the acetic acid solution exhibit the conductivity enhancement. A study of more detailed mechanism for the conductivity enhancement and depression is now under way.

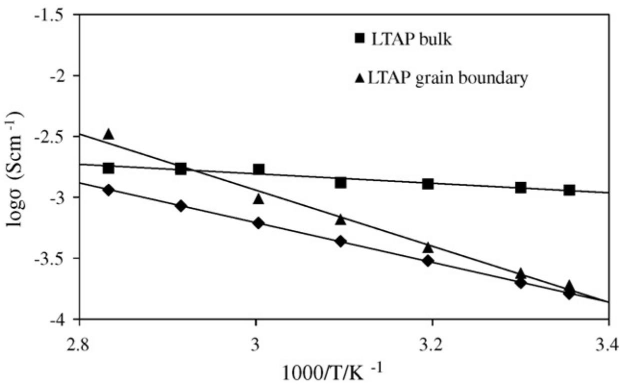

Fig. 4. Temperature dependence of total electrical conductivity, grain boundary conductivity, and bulk conductivity of the sintered pristine LTAP tablet.

The temperature dependence of the total electrical conductivity (σ_t), bulk conductivity (σ_b) and the grain boundary conductivity (σ_g) of the pristine sintered LTAP tablet is shown in Fig. 4, and that of the sintered LTAP tablet immersed in HAc (90 v/o)–H_2O (10 v/o)–LiAc (saturated) for 3 weeks at 50 °C in Fig. 5. The activation energies for the bulk conduction and the grain boundary conduction for the pristine LTAP were calculated from the slope of log σ vs. the inverse of absolute temperature curve to be 10 kJ mol^{-1} and 39 kJ mol^{-1}, respectively. The activation energy for the grain boundary conductivity is comparable with those for previously reported total conductivity of LTAP [11]. The low activation energy for the bulk conductivity of LTAP could be explained by the three dimensional Li^+ ion transport in the NASICON-type structure [13]. On the other hand, the activation energy for the grain boundary conductivity of the LTAP immersed in HAc (90 v/o)–H_2O (10 v/o)–LiAc (saturated) for 3 weeks at 50 °C is calculated to be 60 kJ mol^{-1} in the low temperature range and 134 kJ mol^{-1} in the

Table 1
Electrical conductivity data for the sintered LTAP tablet immersed in HAc (90 v/o)–H_2O (10 v/o)–saturated LiAc and HFc (90 v/o)–H_2O (10 v/o)–saturated LiFc at 50 °C for 3 weeks.

Sintered temperature (°C)	Solution	Electrical conductivity at room temperature (S cm^{-1})	
		Before immersion	After immersion
800	HAc–H_2O–LiAc	3.43×10^{-5}	1.50×10^{-4}
900	HAc–H_2O–LiAc	5.46×10^{-5}	2.52×10^{-4}
1000	HAc–H_2O–LiAc	1.48×10^{-4}	4.77×10^{-4}
1000	HFc–H_2O–LiFc	1.48×10^{-4}	1.40×10^{-4}

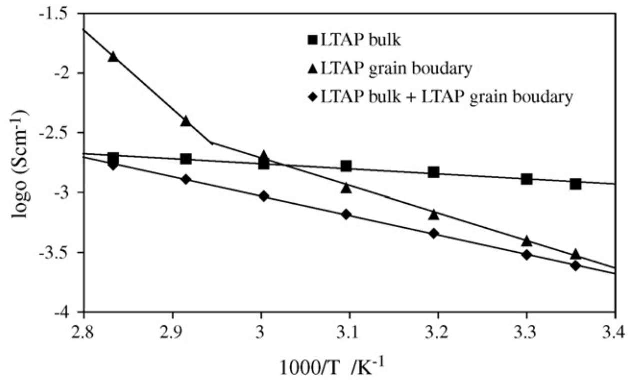

Fig. 5. Temperature dependence of total electrical conductivity, grain boundary conductivity, and bulk conductivity of the sintered LTAP tablet immersed in HAc (90 v/o)–H_2O (10 v/o)–LiAc (saturated) at 50 °C for 3 weeks.

high temperature range. The high activation energy in the high temperature range for the LTAP immersed in acetic acid suggest two types of grain boundary phase in the sintered tablet. A phase with a high resistance at the grain boundary may be removed in the acetic acid solution.

The sintered LTAP tablets are stable in formic acid solution and show no conductivity change by being immersed in the solution at 50 °C for 3 weeks. The electrochemical stability of these solutions is important for the rechargeable lithium–air cell. Especially, the oxidation potentials of CH_3COO^- and $HCOO^-$ should be higher than that of OH^-. Fig. 6 shows the cyclic voltammograms for Pt-black/HAc (90 v/o)–H_2O (10 v/o)–LiAc (saturated)/Pt-black and Pt-black/HFc (95 v/o)–H_2O (5 v/o)–LiFc (saturated)/Pt-black at room temperature. The formic acid solution decomposes electrochemically at a low potential below the OH^- decomposition potential. Therefore, formic acid solution is not acceptable for active materials on the air electrode in rechargeable Li–air batteries. The acetic acid solution is acceptable, however, for Li–air batteries. The Li/polymer electrolyte/LTAP/HFc (95 v/o)–H_2O (5 v/o)–saturated LiFc/Pt, air cell and the Li/polymer electrolyte/LTAP/HAc (90 v/o)–H_2O (10 v/o)–saturated LiAc/Pt, air cell showed open-circuit voltages (OCV) of 3.0 V, and 3.69 V, respectively, which are compared to 3.8 V in the Li/polymer electrolyte/LTAP/aqueous 1 M LiCl/Pt, air cell [14]. The polymer electrolyte of $PEO_{18}Li(CF_3SO_2)_2N$ was used to protect the reaction of lithium metal and the LTAP [6]. The cell reaction for the cell with acetic acid solution could be explained by reaction (2). The calculated OCV from the above reaction is 4.07 V at 25 °C, assuming that the activity of Li^+ in the PEO electrolyte is unity, and oxygen partial pressure on the Pt electrode is 0.2 atm. The low OCV in the cell with aqueous LiCl and acetic acid solution could be explained by a low lithium ion activity in the PEO electrolyte, a low oxygen partial pressure on the Pt electrode, and the junction potentials between the PEO electrolyte and LTAP, and between LTAP and the liquid electrolyte. The low OCV for Li/air cell with formic acid could be explained by the electrochemical reaction of formic acid.

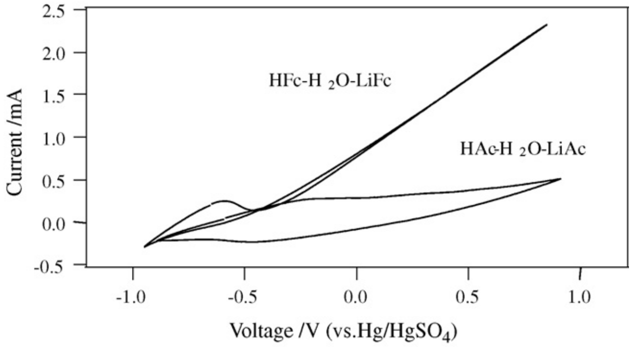

Fig. 6. Cyclic voltammograms of Pt-black/HAc (90 v/o)–H_2O (10 v/o)–saturated LiAc/Pt-black (A) and Pt-black/HFc (95 v/o)–H_2O (5 v/o)–saturated LiFc/Pt-black (B) at room temperature.

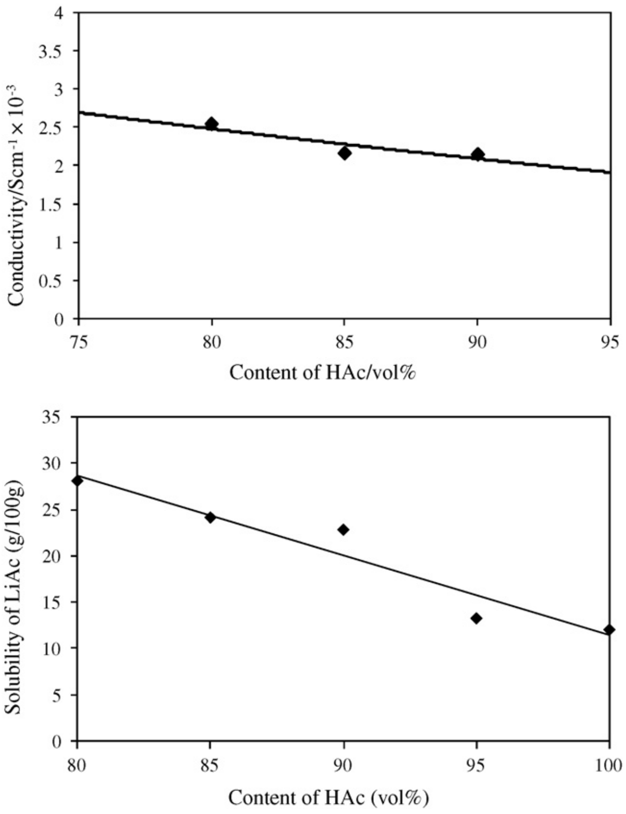

Fig. 7. Electrical conductivity of HAc–H_2O–saturated LiAc and the content of Li^+ ion as a function of the content of H_2O at room temperature.

For the practical application of the acetic acid solution for Li/air batteries, the conductivity of this solution should be high. The electrical conductivities of the HAc–H_2O–LiAc (saturated) system at room temperature are shown as a function of content of HAc in Fig. 7. The solubility of LiAc into HAc–H_2O is shown in this figure. The electrical conductivity of HAc–H_2O–LiAc (saturated) is about $2 \times 10^{-3}\,\mathrm{S\,cm^{-1}}$ and increases slightly with decreasing HAc content. The conductivity is slightly lower than that of the conventional electrolyte for lithium ion batteries, but it is acceptable for the practical applications in batteries. The solubility of LiAc in HAc–H_2O increases with decreasing HAc content. The solubility of LiAc in HAc (90 v/o)–H_2O (10 v/o) is 23 g per 100 ml of solution at room temperature. The solubility limit may affect the cell performance and thus we are currently studying the phase diagram of HAc–H_2O–LiAc.

4. Conclusion

The stability of the water-stable NASICON-type lithium ion conducting solid glass ceramics, LTAP, in acetic acid and formic acid solutions was examined. XRD patterns of the LTAP powder immersed in both solutions at 50 °C for 3 weeks showed no change. The electrical conductivity of the sintered samples immersed in HAc (90 v/o)–H_2O (10 v/o)–LiAc (saturated) at 50 °C for 3 weeks was enhanced. No conductivity change was observed for the sintered samples immersed in HFc (90 v/o)–H_2O (10 v/o)–LiFc (saturated) at 50 °C for 3 weeks. The cyclic voltammogram of the acetic acid solution showed no decomposition of CH_3COO^-, but formic acid was electrochemically decomposed at a low potential. That is, the formic acid solution cannot be used as an active material in the air electrode for a rechargeable lithium–air cell. The acetic acid is an excellent candidate for the active material in an air electrode, because the water-stable lithium ion conducting solid electrolyte is stable in acetic acid solution, and acetic acid is electrochemically stable at a high potential. The calculated energy density from $2Li + 2CH_3COOH + 1/2O_2 = 2CH_3COOLi + H_2O$ is as high as 1477 Wh kg^{-1}. This high calculated energy density suggests the possibility of developing a battery with 600 Wh kg^{-1} in a Li/LTAP/aqueous acetic acid/air system.

Acknowledgments

The authors thank OHARA Inc., for supplying the LTAP plates and powder and are grateful to Dr Y. Inda of OHARA Inc., for his helpful comments and suggestions.

This research was sponsored by the New Energy and Industrial Technology Development Organization (NEDO) of Japan under the project, Development of High Performance Battery System for Next-generation Vehicles.

References

[1] M. Armand, J.-M. Tarascon, Nature 451 (2008) 652.
[2] K.M. Abraham, Z. Jiang, J. Electrochem. Soc. 143 (1996) 1.
[3] A. Ogasawara, A. Debart, M. Holtzapfel, P. Novak, P.J. Bruce, J. Am. Chem. Soc. 129 (2006) 1390.
[4] S.R. Younesi, K. Ciosek, K. Edstrom, in: 214th Electrochemical Society Meeting Abstract #465, Honolulu, USA, 2008.
[5] N. Imanishi, S. Hasegawa, T. Zhang, A. Hirano, Y. Takeda, O. Yamamoto, J. Power Sources 185 (2008) 1392.
[6] T. Zhang, N. Imanishi, S. Hasegawa, A. Hirano, J. Xie, Y. Takeda, O. Yamamoto, N. Sammes, J. Electrochem. Soc. 155 (2008) A965.
[7] S. Hasegawa, N. Imanishi, T. Zhang, J. Xie, A. Hirano, Y. Takeda, O. Yamamoto, J. Power Sources 189 (2009) 371.
[8] J. Fu, Solid State Ionics 96 (1997) 195.
[9] X. Xu, Z. Wen, J. Wu, X. Yang, Solid State Ionics 178 (2007) 29.
[10] P.G. Bruce, A.R. West, J. Electrochem. Soc. 130 (1983) 652.
[11] M. Cretin, F. Fabry, J. Eur. Ceram. Soc. 19 (1999) 2931.
[12] X.M. Wum, X.H. Li, Y.H. Zhang, M.F. Xu, Z.Q. He, Mater. Lett. 58 (2004) 1227.
[13] H.Y.-P. Hong, Mater. Res. Bull. 11 (1976) 173.
[14] T. Zhang, N. Imanishi, S. Hasegawa, A. Hirano, J. Xie, Y. Takeda, O. Yamamoto, N. Sammes, Electrochem. Solid State Lett. 12 (2009) A132.