J Mater Sci (2010) 45:3954–3956
DOI 10.1007/s10853-010-4522-4

LETTER

Stability predictions of solid Li-ion conducting membranes in aqueous solutions

J. Wolfenstine

Received: 2 March 2010 / Accepted: 12 April 2010 / Published online: 27 April 2010
© US Army Research Laboratory 2010

Recently, there has been interest in the development of Li–Air batteries for high energy applications. One configuration involves the use of a Li anode in a non-aqueous electrolyte which is separated from an aqueous electrolyte containing the air cathode by a solid state Li-ion conducting membrane [1, 2]. One of the major requirements for the membrane material besides high Li-ion conductivity is water stability. Currently the Li-ion conducting membrane of choice is based on the NASICON structure of the type $Li_{1+x}M_xTi_{2-x}(PO_4)_3$ (M = Al, Sc, Y, La) with $x \sim 0.3$ [3–6]. The composition of choice for the membrane is $Li_{1+x+y}Al_xTi_{2-x}Si_yP_{3-y}O_{12}$ [LATP] with $x \sim 0.3$ and $y \sim 0.2$ [3–7]. The LATP membrane is usually formed by a glass–ceramic processing technique. Silicon is added to improve the fluidity and thermal stability of the melt [3, 7]. The chemical stability of LATP supplied by Ohara Inc., Japan as a function of pH has been investigated by Hasegawa et al. [6]. They observed there was no significant difference in the X-ray diffraction patterns after immersion in distilled water for one month. Hasegawa et al. [6] also observed that the total resistance (sum of lattice and grain boundary resistances) of $Li_{1+x+y}Al_xTi_{2-x}Si_yP_{3-y}O_{12}$ increased by about a factor of 1.4 after 1 month in distilled water. The lattice resistance remained unchanged. They suggested that the change in total resistance was due to formation of a new phase at the grain boundary [6]. Hasegawa et al. observed that LATP was stable in aqueous solutions of 1 M $LiNO_3$ and 1 M LiCl with pH $\sim$ 6 and unstable in 0.1 M HCl (pH $\sim$ 1) and 1 M LiOH (pH $\sim$ 14). Very recently, Zhang et al. [3] investigated LATP immersed in an acetic acid solution (pH $\sim$ 4) at 50°C for 3 weeks. They observed no change in the X-ray diffraction pattern with a slight decrease in electrical conductivity. Recently, Wolfenstine et al. [8] investigated the water stability (pH $\sim$ 7) of another promising Li-ion conducting membrane material, $Li_{0.33}La_{0.57}TiO_3$ [LLTO]. $Li_{0.33}La_{0.57}TiO_3$ has a reported bulk Li-ion conductivity equally to if not greater than LATP [9, 10]. Wolfenstine et al. [8] observed using dense LLTO that the X-ray diffraction pattern and ionic conductivity remained unchanged after immersion in distilled water for a period of 1 month. In addition, current work in progress by Wolfenstine has compared the stability of dense $Li_{0.33}La_{0.57}TiO_3$ to LATP obtained from Ohara Corporation, Japan. The results of the pH, X-ray diffraction, weight loss, chemical analysis, and microhardness measurements reveal that both $Li_{0.33}La_{0.57}TiO_3$ and $Li_{1+x+y}Al_xTi_{2-x}P_{3-y}Si_yO_{12}$ were relatively stable in a water environment (pH $\sim$ 7). From the above experimental results it appears that $Li_{0.33}La_{0.57}TiO_3$ and $Li_{1+x+y}Al_xTi_{2-x}P_{3-y}Si_yO_{12}$ have reasonable chemical stability in aqueous solutions in a middle pH range (4–7) but are unstable at low and high pH values.

It is the purpose of this note to compare the above experimental results on the stability of $Li_{0.33}La_{0.57}TiO_3$ and $Li_{1+x+y}Al_xTi_{2-x}P_{3-y}Si_yO_{12}$ in aqueous solutions to thermodynamic predictions based on a simple Potential–pH (Pourbiax) diagram for water to determine if the Potential–pH diagram can be used to predict the stability of a solid Li-ion conducting membrane in aqeous solutions.

Li et al. [11] constructed Potential–pH (Pourbiax) diagrams referenced to the Li^+/Li potential to determine a Li-containing materials stability in aqueous solutions for two different charge neutrality conditions; $[Li^+] = 1$ M and $[Li^+] = [OH^-]$. Li et al. [11] observed for $LiMn_2O_4$ in

---

J. Wolfenstine (✉)
Army Research Laboratory, RDRL-SED-C, 2800 Powder Mill Road, Adelphi, MD 20783, USA
e-mail: jwolfenstine@arl.army.mil;
jeff.wolfenstine@us.army.mil

a 1 M LiOH aqueous electrolyte that the experimentally results were in very good agreement with stability predictions from the Potential–pH diagram. The reaction for a Li-containing material in water is as follows [11]:

$$\text{Li (intercalated)} + H_2O \leftrightarrow Li^+ + OH^- + 1/2H_2 \quad (1)$$

From Eq. 1 for a Li-containing material not to react with water (stable) implies no hydrogen gas will be evolved [11, 12]. If a Li-containing material reacts with water to form hydrogen gas then it is considered unstable [11, 12]. The voltage (versus Li^+/Li) for hydrogen evolution as a function of pH for two different charge neutrality conditions; $[Li^+] = [OH^-]$ and $[Li^+] = 1$ M are shown in Figs. 1 and 2, respectively [11]. For voltages below the line hydrogen will be evolved (unstable), whereas above the line no hydrogen will be evolved (stable). From Figs. 1 and 2 it is observed that as pH increases the hydrogen evolution voltage decreases. It should be noted for aqueous electrolytes there is also a higher voltage stability limit (1.23 V above the hydrogen evolution voltage) that corresponds to oxygen gas evolution [11, 12]. Above this line oxygen gas evolution occurs. The oxygen evolution voltage is not plotted on Figs. 1 and 2 because for most of the current Li-ion conducting solid membranes their voltage is low (see following paragraph), so that it is the hydrogen evolution voltage that determines their stability in aqueous solutions.

We can use Figs. 1 and 2 as a guide to predict if $Li_{1+x+y}Al_xTi_{2-x}P_{3-y}Si_yO_{12}$ and $Li_{0.33}La_{0.57}TiO_3$ will be stable/unstable with in aqueous electrolytes if their voltage versus Li/Li^+ is known. At present the voltage for $Li_{1+x+y}Al_xTi_{2-x}P_{3-y}Si_yO_{12}$ versus Li^+/Li is unknown. However, a Li insertion/extraction voltage does exist for $LiTi_2(PO_4)_3$ [12]. For Li insertion/extraction into $LiTi_2(PO_4)_3$ Delmas et al. [13] have shown that the open circuit voltage for $Li_{1.3}Ti_2(PO_4)_3$ is ~2.5 V versus Li/Li^+. For Li insertion/extraction into $Li_{0.29}La_{0.57}TiO_3$ close to equilibrium conditions Birke et al. [14] observed the voltage for $Li_{0.33}La_{0.57}TiO_3$ is ~1.6 V versus Li/Li^+. In a first approximation we can use these voltages to predict the stability of $Li_{0.33}La_{0.57}TiO_3$ and $Li_{1+x+y}Al_xTi_{2-x}P_{3-y}Si_yO_{12}$ in aqueous electrolytes. The voltages of $Li_{1+x+y}Al_xTi_{2-x}P_{3-y}Si_yO_{12}$ (~2.5 V versus Li/Li^+) and $Li_{0.33}La_{0.57}TiO_3$ (~1.6 V versus Li/Li^+) as a function of pH are shown in Figs. 1 and 2 as dotted lines. Also included in Figs. 1 and 2 for the two different charge neutrality conditions is the voltage of the two materials versus Li/Li^+ as function of pH [11]. For the charge neutrality condition $[Li^+] = [OH^-]$ (Fig. 1) it is observed for $Li_{0.33}La_{0.57}TiO_3$ its voltage is below the hydrogen evolution voltage over the entire pH range and hence, it is predicted to be unstable over this pH range. For $Li_{1+x+y}Al_xTi_{2-x}P_{3-y}Si_yO_{12}$ its voltage is above the hydrogen evolution line above a pH ~ 11 and hence, above pH ~ 11 it is predicted to be stable (no hydrogen evolution). For the charge neutrality condition $[Li^+] = 1$ M (Fig. 2) it is observed for $Li_{0.33}La_{0.57}TiO_3$ again its voltage is below the hydrogen evolution voltage over the entire pH range and hence, it is predicted to be unstable over this pH range. For $Li_{1+x+y}Al_xTi_{2-x}P_{3-y}Si_yO_{12}$ its voltage is above the hydrogen evolution line above a pH ~ 8 and hence, above pH ~ 8 it is predicted to be stable (no hydrogen evolution). From Figs. 1 and 2 for $Li_{1+x+y}Al_xTi_{2-x}P_{3-y}Si_yO_{12}$ it can be observed that increasing the Li^+ concentration has increased the pH stability range to lower values (11–8). This result is expected from Eq. 1, which predicts that as the Li^+ concentration increases the reaction is driven to the

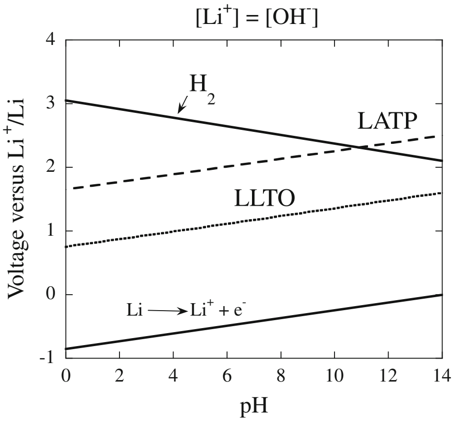

Fig. 1 The H_2 stability region as function of pH [11]. *Below the solid line* is the region where hydrogen evolution occurs (unstable). *Above the solid line* no hydrogen evolution occurs (stable). LLTO is unstable at all pH values from 0 to 14. In contrast, LATP is predicted to be stable at a pH value greater than 11

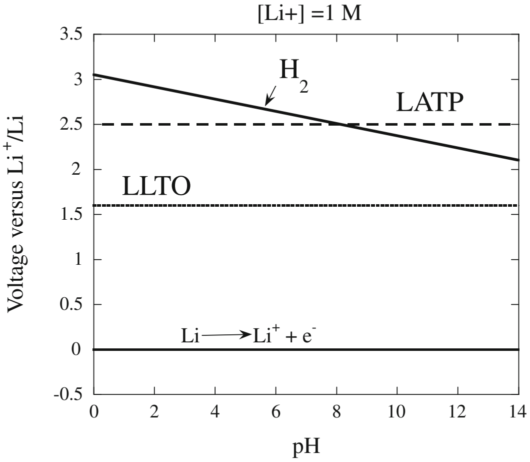

Fig. 2 The H_2 stability region as function of pH [11]. *Below the solid line* is the region where hydrogen evolution occurs (unstable). *Above the solid line* no hydrogen evolution occurs (stable). LLTO is unstable at all pH values from 0 to 14. In contrast, LATP is predicted to be stable at a pH value greater than 8. A comparison of this figure with Fig. 1 reveals that increasing the $[Li^+]$ has increased the stability of LATP

left (reducing the deintercalation tendency of Li from the material).

It is of interest to compare the water stability predictions from Figs. 1 and 2 for $Li_{0.33}La_{0.57}TiO_3$ and $Li_{1+x+y}Al_xTi_{2-x}P_{3-y}Si_yO_{12}$ with the recent experimental results of Hasegawa et al. [6] on $Li_{1+x+y}Al_xTi_{2-x}P_{3-y}Si_yO_{12}$ and Wolfenstine (work in progress) on $Li_{1+x+y}Al_xTi_{2-x}P_{3-y}Si_yO_{12}$ and $Li_{0.33}La_{0.57}TiO_3$. As stated earlier, Hasegawa et al. [6] observed that $Li_{1+x+y}Al_xTi_{2-x}P_{3-y}Si_yO_{12}$ was stable in aqueous solutions of 1 M $LiNO_3$ and 1 M LiCl with pH ~ 6 and unstable in 1 M LiOH with pH ~ 14. Wolfenstine found that $Li_{1+x+y}Al_xTi_{2-x}P_{3-y}Si_yO_{12}$ and $Li_{0.33}La_{0.57}TiO_3$ were relatively stable in distilled water with pH ~ 7. The Potential–pH diagram (Fig. 1) predicts for the charge condition $[Li^+] = [OH^-]$ that both $Li_{0.33}La_{0.57}TiO_3$ and $Li_{1+x+y}Al_xTi_{2-x}P_{3-y}Si_yO_{12}$ should be unstable at pH ~ 7. From Fig. 2 for the charge neutrality condition $[Li^+] = 1$ M the Potential–pH diagram predicts that $Li_{1+x+y}Al_xTi_{2-x}P_{3-y}Si_yO_{12}$ should unstable at pH ~ 6 and stable at pH ~ 14. Consequently, it appears that the experimental results are not in agreement with the stability predictions based on the Potential–pH diagrams. At present the reason(s) for this disagreement are not known. Some possible explanations may include: (1) the samples are unstable but, appear to be stable during the testing times used for the present experiments, in which case long time tests are needed to confirm the true chemical stability in a aqueous environment, (2) the stability of the material is a function of boundary phases, whose composition(s) maybe be different from the bulk material, which are not included in Eq. 1, (3) that there is a reaction between the aqueous solution and the solid Li-ion conducting material leading to the formation of a new phase on the surface of the material that acts as a protective layer that prevents further reaction, similar to the formation of a solid electrolyte interphase (SEI) layer on a graphite anode in a Li-ion battery which forms during the first few cycles as a result of the interaction between the organic electrolyte and graphite [15]. The SEI layer prevents further reaction between graphite and the organic electrolyte. Finally, the Potential–pH diagram correctly predicts the stability of Li (Eq. 1) in aqueous solutions. The instability of the solid Li-ion conducting material is not a result of the reaction between Li and the aqueous solution but, due to the reaction between the aqueous solution and other elements in the solid Li-ion conductor. For example, Zhang and Dahn [16] predict based on the Potential–pH diagram that VO_2 (B) should be stable (no hydrogen evolution) in aqueous solutions at high pH values. At high pH values no hydrogen evolution was exhibited, in agreement with the prediction. However, they observed that VO_2 (B) dissolved into the aqueous electrolyte at high pH values. In addition, Porcher et al. [17] showed for $LiFePO_4$ in aqueous solutions that at the high and low end pH values higher concentrations of both Fe and PO_4 were dissolved into the solutions than at middle pH values. A similar situation could exist for $Li_{1+x+y}Al_xTi_{2-x}P_{3-y}Si_yO_{12}$ and $Li_{0.33}La_{0.57}TiO_3$. Preliminary experiments on $Li_{0.33}La_{0.57}TiO_3$ have shown that when $Li_{0.33}La_{0.57}TiO_3$ was placed in an aqueous solution of pH ~ 14 for 1 month that chemical analysis revealed a higher La content was observed in the aqueous solution, then when $Li_{0.33}La_{0.57}TiO_3$ was immersed in distilled water (pH ~ 7) for 1 month.

In conclusion, it appears that the experimental results for the stability of $Li_{1+x+y}Al_xTi_{2-x}P_{3-y}Si_yO_{12}$ and $Li_{0.33}La_{0.57}TiO_3$ in aqueous solutions are in disagreement with thermodynamic predictions based on a simple Potential–pH diagram. At present reason(s) for this discrepancy are not known. The results of this study suggest that a simple Potential–pH diagram for water to predict the stability of solid Li-ion conducting membranes in aqueous environments is not accurate.

Acknowledgement The author would like to acknowledge support of the U. S. Army Research Laboratory (ARL).

References

1. Kowalczk I, Read J, Salomon M (2007) Pure Appl Chem 5:851
2. Visco SJ, Katz BD, Nimon YS, De Jonghe LC (2007) US Patent 7,282,295 B2
3. Zhang T, Imanishi N, Shimonishi Y, Hirano A, Xie J, Takeda Y, Yamamoto O, Sammes N (2010) J Electrochem Soc 157:A214
4. Zhang T, Imanishi N, Hasegawa S, Hirano A, Xie J, Takeda Y, Yammamoto O, Sammes N (2008) J Electrochem Soc 155:A965
5. Imanishi N, Hasegawa S, Zhang T, Hirano A, Takeda Y, Yamamoto O (2008) J Power Sources 185:1392
6. Hasegawa S, Imanishi N, Zhang T, Xie J, Hirano A, Takeda Y, Yamamoto O (2008) J Power Sources 189:371
7. Fu J (2002) US Patent 6,485,622
8. Wolfenstine J, Allen JL (2008) J Mater Sci 43:7247. doi:10.1007/s10853-008-3048-5
9. Kawai H, Kuwano J (1994) J Electrochem Soc 141:L74
10. Stramare S, Thangadurai V, Weppner W (2003) Chem Mater 15:3974
11. Li W, McKinnon WR, Dahn JR (1994) J Electrochem Soc 141:2310
12. Li W, Dahn JR, Wainwright S (1994) Science 264:1115
13. Delmas C, Nadri A, Soubeyroux JL (1988) Solid State Ionics 28–30:419
14. Birke P, Scharner P, Huggins RA, Weppner W (1997) J Electrochem Soc 144:L167
15. Xu K (2004) Chem Rev 104:4303
16. Zhang M, Dahn JR (1996) J Electrochem Soc 143:2730
17. Porcher W, Moreau P, Lestriez B, Jouanneau S, Guymord D (2008) Electrochem Solid State Lett 11:A4