H$^+$ diffusion and electrochemical stability of Li$_{1+x+y}$Al$_x$Ti$_{2-x}$Si$_y$P$_{3-y}$O$_{12}$ glass in aqueous Li/air battery electrolytes

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HIGHLIGHTS

► H$^+$-ion diffusion in LATP glass and the interactions with the glass surface were investigated.
► Protons can be adsorbed on the LATP glass surface but cannot go through the glass.
► The observed cathodic current is attributed to H$^+$ adsorption/reaction on LATP.
► LATP glass surface will be seriously corroded in a strong alkaline electrolyte with time.
► Appropriate electrolytes are needed for long-term operation of aqueous Li–air batteries.

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ABSTRACT

It is well known that LATP (Li$_{1+x+y}$Al$_x$Ti$_{2-x}$Si$_y$P$_{3-y}$O$_{12}$) glass is a good lithium (Li)-ion conductor. However, the interaction between LATP glass and H$^+$ ions in aqueous electrolytes (including the diffusion and surface adsorption of H$^+$ ions) needs to be well understood before the long-term application of LATP glass in an aqueous electrolyte can be realized. In this work, we investigate H$^+$-ion diffusion in LATP glass and their interactions with the glass surface using both experimental and modeling approaches. Our results indicate that the apparent H$^+$-related current observed in the initial cyclic voltammetry scan should be attributed to the adsorption of H$^+$ ions on the LATP glass rather than the bulk diffusion of H$^+$ ions. Furthermore, density functional theory calculations indicate that the H$^+$-ion diffusion energy barrier (3.21 eV) is much higher than that for Li$^+$ ions (0.79 eV) and Na$^+$ ions (0.79 eV) in a NASICON-type LiTi$_2$(PO$_4$)$_3$ material. As a result, H$^+$-ion conductivity in LATP glass is negligible at room temperature. However, significant surface corrosion was found after the LATP glass in a strong alkaline electrolyte. Therefore, to prevent LATP glass from corrosion, appropriate electrolytes must be developed for long-term operation of LATP in aqueous Li–air batteries.

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1. Introduction

Li–air batteries have attracted intensive attention worldwide in recent years because they exhibit the highest theoretical specific energy among various electrochemical energy-storage systems [1]. Although intensive work has been done on the rechargeability of Li–air batteries with non-aqueous electrolytes [2–4], results reported in the last two years have revealed that most of the apparent reversible reactions reported previously for Li–air batteries with non-aqueous electrolytes result from decomposition of the electrolyte rather from the Li–O$_2$ reaction [5–8]. Apparently, the stabilities of all components in Li–air batteries, including batteries that use non-aqueous and aqueous electrolytes, need to be carefully investigated for their long-term application.

In the case of Li–air batteries that use an aqueous electrolyte, protection of the lithium-metal electrode is critical. Solid-state electrolytes, such as LATP (Li$_{1+x+y}$Al$_x$Ti$_{2-x}$Si$_y$P$_{3-y}$O$_{12}$) glass made by Ohara Corp. of Japan, have good Li-ion conductivity ($\sim 2 \times 10^{-4}$ S cm^{-1}) and are impermeable to water. Unfortunately, LATP glass is not stable when in contact with Li metal. Visco and co-workers [9] first solved this problem by depositing a solid-state interfacial layer (e.g., Cu$_3$N, Lipon, etc.) between the Li metal and the LATP glass, thus forming a protected lithium electrode (PLE). The combination of PLEs with different liquid electrolytes has been

used in various forms of Li–air batteries [10–12]. It is expected that rechargeable Li–air batteries using aqueous electrolytes could be practically applied if the LATP glass-based solid electrolyte is stable in the aqueous electrolyte (in which H$^+$ ions are always present) during long-term electrochemical cycling.

Several groups [9–12] have reported aqueous Li–air battery systems with PLE technology. However, no systematic investigation has been reported on the electrochemical stability of LATP glass in various aqueous electrolytes. It is well known that the proton exhibits the same charge value as a Li$^+$ ion, and its particle size is even smaller than that of a Li$^+$ ion. On the other hand, several groups have published results about the dual-ion (i.e., Li$^+$ and H$^+$ ions) solid electrolyte [13–16] and the NASICON structure, H$^+$-ion conductive material [17–19]. In an aqueous electrolyte, regardless of its pH value, H$^+$ ions always are present. These protons may react with the LATP glass either chemically or electrochemically and may have a profound effect on the long-term electrochemical stability of the glass. Therefore, before LATP glass can be used on a long-term basis in Li–air batteries, we need a better understanding of the interaction between H$^+$ ions and the glass and the possible diffusion of H$^+$ ions in the glass. Recently, we conducted several special experiments to investigate the effect of the protons on the electrochemical stability of LATP glass in various aqueous electrolytes. Density functional theory calculations also were performed to investigate the conductivity of various ions in LATP glass. Details of our experimental and theoretical analyses and the results obtained are reported in this paper.

2. Experimental

LATP glass was purchased from OHARA Corp. (Japan) and used as received. For the electrochemistry test, LATP glass was fabricated into the PLE as described by He et al. [11]. The interlayer liquid electrolyte between the Li metal and the LATP glass was 1-M LiPF$_6$ in PC-DMC (3:7 ratio by volume) solvent. Fig. 1 is a photograph of the PLE prepared by this method. The PLE was used as the working electrode in cyclic voltammetry (CV) and constant current tests. Platinum (Pt) foil and an Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. Aqueous solutions (1-M) of LiCl, LiOH, and HCl were used as electrolytes in these experiments. The electrochemical performance of the LATP glass was measured with an electrochemistry workstation (CHI 660C). The voltage range for CV scans was between −1 V and +1 V vs. open circuit voltage (OCV), and the scan rate was 5 mv s^{-1}. Each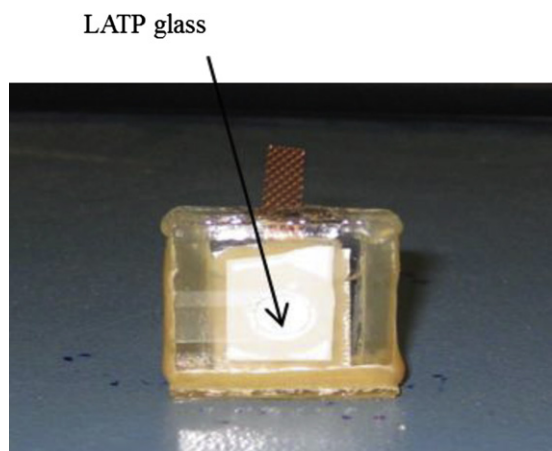 CV scan was directed first toward catholic polarization and then toward anodic polarization. The surface morphologies of the LATP glasses immersed in different electrolytes were examined by scanning electron microscopy using a JEOL 5900 Scanning Electron Microscope at a working distance of 12 mm and an accelerating voltage of 20 keV.

The variation of H$^+$-ion concentrations in the electrochemical cells during electrochemical testing was monitored in a specially designed two-chamber container operated in a nitrogen atmosphere. Fig. 2 shows the schematic structure of the test container. The glass container was separated into two chambers (labeled as A and B) by an unprotected fresh LATP glass. An aqueous electrolyte (25 mL, 1-M LiCl) was added to each chamber. Two PLEs prepared by the method described above were placed in the two chambers and were used to provide constant current. A pH meter was used to measure the H$^+$-ion concentration in the chamber. Two sets of these experimental units were prepared with fresh LATP glass and fresh LiCl electrolyte. One unit was used to monitor the variation of the H$^+$-ion concentration without current passing through the chambers, and the other unit was used to monitor the variation of the H$^+$-ion concentration when a current of 0.4 mA was passed continuously through the two chambers and two PLE electrodes. Both tests lasted about 50 h, which was long enough for a pH change to occur if H$^+$ ions could move from chamber A to chamber B.

Direct-current (DC) polarization measurements reported by Zhu and Mellander [15] were used to verify if there is H$^+$-ion diffusion in the LATP glass. In this approach, Pt paste was painted on both sides of the LATP glass. The sample was tested in a hydrogen (H$_2$) atmosphere chamber at room temperature to form a cell with a structure of (H$_2$)Pt/LATP glass/Pt (H$_2$). A constant voltage (3 V) was applied across this sample for 10 min at which time the polarization current had stabilized. Then, the polarity of the applied voltage was reversed, and the current level was measured as a function of time.

The diffusion barriers for the H$_2$, Li, and sodium (Na) ions in LiTi$_2$(PO$_4$)$_3$ were determined using density functional theory calculations as implemented in the Vienna ab initio package [20] with a plane wave basis set. The projector augmented wave method [21] was used to describe electron–ion interaction, while the generalized gradient approximation using the Perdew–Burke–Ernzerhof function was used to describe the electron-exchange correlation. We used a plane wave basis set to an energy cutoff of 400 eV. Computations were based on a 1 × 1 × 1 supercell (consisting of 108 atoms) with a 3 × 3 × 3 Monkhorst–Pack [22] mesh for the k-point sampling. Saddle-point structures and associated minimum energy pathways were computed with the climbing-image nudged elastic band method [23]. After all degrees of freedom of each structure were optimized, the transition state search began with a nudged elastic band
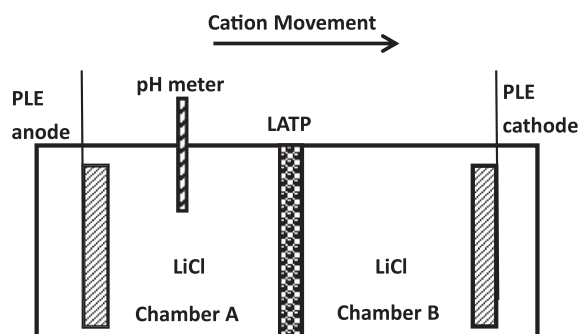

Fig. 1. Photograph of a PLE prepared in this work.

Fig. 2. Schematic of experimental setup to test H$^+$-ion concentration variations as a function of time.

calculation, which involved a chain of images (five in our calculations) initially determined through linear interpolation from the fixed initial and final configurations.

3. Results and discussion

The value and direction of the current observed in a CV scan have been widely used to investigate ion movement in an electrochemical cell. In a typical CV scan of the PLE vs. Pt foil (with Ag/AgCl as the reference electrode), an appreciable cathodic current implies that some cations may move through the LATP glass from the aqueous electrolyte and then deposit on the Li metal. This approach has been used to investigate the possible H$^+$-ion conductivity in LATP glass. Fig. 3 shows the CV test results of a PLE cell (with LATP glass protection) in different aqueous electrolytes. The open circuit potential (OCP) of the PLE is −3.36 V in HCl solution, −3.19 V in LiCl solution and −3.19 V in LiOH solution, all are referenced to the Ag/AgCl electrode. The small difference of the OCP in HCl solution from that in LiCl and LiOH solutions is probably due to the slight difference of the PLE surface conditions in the different electrolyte solutions.

Obviously, as shown in Fig. 3, when an electrolyte with Li$^+$ ions (i.e., LiOH or LiCl solutions) was used, the CV curves of PLEs show symmetric behavior with high current densities. During a cathodic scan, Li$^+$ ions in the electrolyte move through the LATP glass and are deposited on Li metal inside the PLE electrode. During an anodic scan, Li$^+$ ions inside the PLE move through the LATP glass and return to the electrolyte. The scan curve is symmetric relative to the OCP because Li$^+$ ions are present both inside and outside of the PLE.

As a comparison, when an electrolyte without Li$^+$ ions (such as an HCl solution that only contains H$^+$ cation) was used and the PLE/Pt cell was scanned initially in the cathodic direction, the initial cathodic current, if any, should be attributed to H$^+$ ions. As shown in Fig. 3, a small cathodic current was observed during the initial cathodic scan. This current results from either the diffusion of H$^+$ ions through the LATP glass or from surface adsorption/reaction of H$^+$ ions with the LATP glass because there are no Li$^+$ ions present in the electrolyte during the initial scan.

To explore the origin of the cathodic current observed in the above experiment, we conducted a special experiment (see Fig. 2) to test the variation of H$^+$-ion concentrations in two reaction chambers. One PLE in chamber A was the anode, and the other PLE in chamber B was the cathode. When a current is supplied to the two electrodes in this experimental setup, Li$^+$ ions will move from chamber A and pass through the LATP glass to chamber B. If H$^+$ ions could pass through the LATP glass from chamber A to chamber B, we expected that the H$^+$-ion concentration in chamber A would continuously change during the electrochemical process. A pH meter was used to detect changes in the H$^+$-ion concentration. A 1-M LiCl solution was used as the electrolyte because a stable current could be obtained in a Li$^+$-ion electrolyte; therefore, it would be possible to measure, if exists, H$^+$-ion conductivity during the longer test. In addition, a small pH change can be detected easily in a neutral solution.

Variation of pH values in chamber A as a function of time is shown in Fig. 4. The solid square symbols in Fig. 4 show the time dependence of the pH value of a LiCl aqueous solution in chamber A during the electrochemical process. We found that the pH value in chamber A increased with time but eventually stabilized after about 20 h. On the other hand, even with no applied current, the pH value of the chamber A still increased to the same stable value as the cells with applied current. These results show that the final H$^+$-ion concentration in the chambers is independent of the electrochemical process. Therefore, pH variation in the chambers can be attributed to H$^+$-ion adsorption, ion exchange, and/or surface etching rather than H$^+$ diffusion through the glass, which would lead to a continuous pH value change instead of a stabilized pH value. Fig. 4 also reveals that the pH in chamber A stabilized quickly when a current was imposed (∼20 h vs. ∼50 h). This means that the electrochemical process accelerates the surface chemical equilibrium process mentioned above.

To further investigate possible H$^+$-ion diffusion in the LATP glass, the DC polarization method reported by Zhu and Mellander [15] was used to investigate the possible H$^+$-ion diffusion in LATP glass. The polarization curve for LATP glass is shown in Fig. 5. The inset in Fig. 5 is the typical direct-current polarization curve in a hydrogen atmosphere for a solid electrolyte with two kinds of mobile ionic species (i.e., Li$^+$ and H$^+$ ions). The current plateau of region B was attributed to steady H$^+$-ion transport [15,16]. It is known that LATP glass is a Li$^+$-ion conductor. If it can also conduct H$^+$-ion a current plateau similar to that shown in Fig. 5 inset should be observed. However, no current plateau corresponding to H$^+$-ion diffusion is observed in the DC polarization curve of the LATP glass as shown in Fig. 5. This result is a clear evidence that there is little H$^+$-ion diffusion in LATP glass at room temperature. Therefore, the apparent cathodic current observed during the initial scan of PLE/Pt cell shown in Fig. 3 should be attributed to H$^+$ adsorption/reaction on LATP glass surface rather than H$^+$ conduction through the glass.
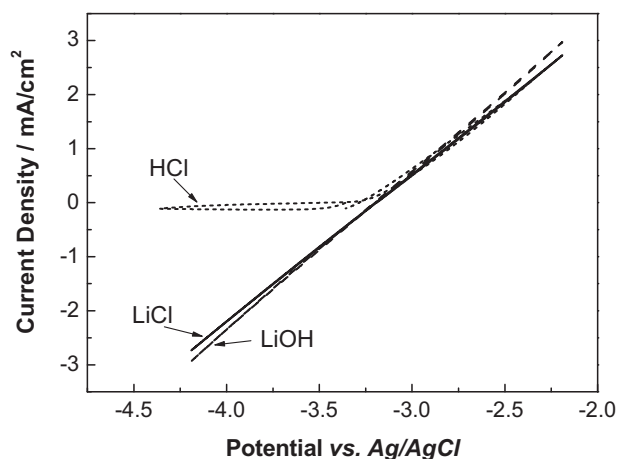
Fig. 3. CV tests of PLEs in different aqueous electrolytes. The OCPs of the PLE are −3.36 V, −3.19 V and −3.19 V vs. Ag/AgCl in HCl solution, LiCl solution and LiOH solution, respectively.
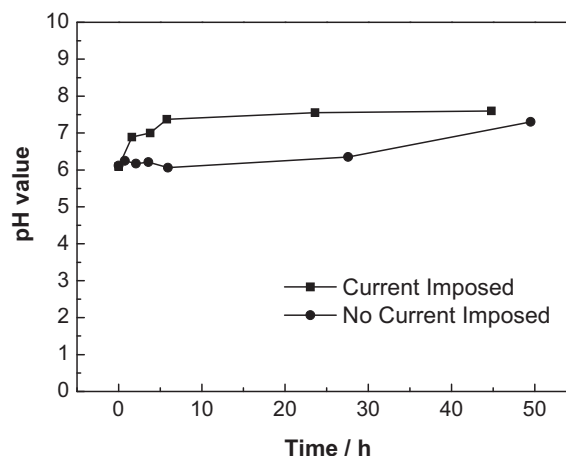
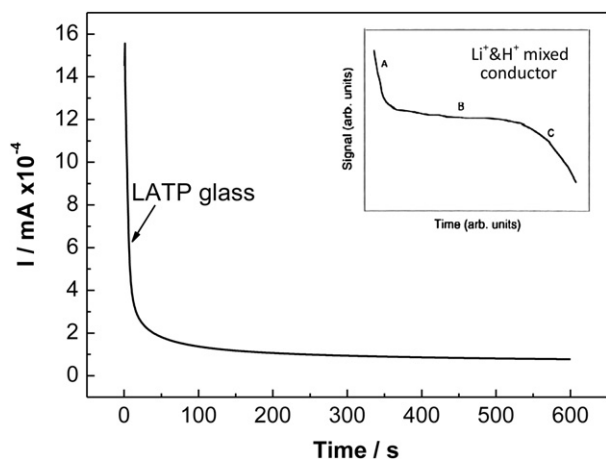**Fig. 4.** Variation of pH values in chamber A as a function of time.

Fig. 5. DC (3 V) polarization curve of LATP glass in an H_2 atmosphere (the inset is the typical DC polarization curve of Li^+ and H^+ ion conductive solid electrolytes).

temperatures or electrical effects [26]. Herein, the ability of Li^+ (Na^+) and H^+ ions to diffuse from the M1 site to the M2 site and the corresponding energy paths are calculated. Fig. 6(a) and (b) shows the diffusion path of Li^+ (Na^+) and H^+ ions, respectively, which does not follow a straight line. Li^+ and Na^+ ions take a "zig-zag" path in three dimensions [28]. While H^+ ion does not diffuse along the same path as Li^+ ion and Na^+ ion, it will diffuse near the oxygen due to the strong interaction between H^+ and oxygen. Fig. 6(c) and (d) shows energy barriers of Li^+ (Na^+) and H^+ ions in a typical NASICON glass, respectively. The energy barriers are all calculated relative to the most stable positions; that is the M1 for Li^+ (Na^+) and Mid-M for H^+ ions. The energy barriers of Li^+ and Na^+ ions are determined to be 0.79 and 0.82 eV, respectively. Both are higher than the experimental activation energies reported by Paris et al. [26] and Mouahid et al. [27] However, the tendency of energy barriers for Li^+ and Na^+ ions obtained from the calculation is consistent with the experimental results, i.e., the activation energy of Li^+ is less than that of Na^+. In addition, both calculated values are very close, same as the experimental data. The minor differences between the computational results and the experimental results are well within the limitation of modeling itself (i.e., the limited numbers of the atoms involved in calculation).

Contrast to the energy barriers of Li^+ and Na^+ ions, the energy barriers of the H^+ ion is 3.21 eV, which is much higher than that of Li^+ and Na^+ ions. Apparently, it is much more difficult for H^+ ions to diffuse through the NASICON-type glass structure. To explore the physical origin why H^+ has much lower diffusion ability in this material, the charge density iso-surfaces of $LiTi_2(PO_4)_3$ with H^+ ions at the M1 and Mid-M sites are shown in Fig. 6(e) and (f), respectively. From the figure, it is clear that the H^+-ion interacts with nearby oxygen as it moves close to the Mid-M site, forming a strong bond with the oxygen. The dissociation of H^+ from oxygen requires a much higher energy, which leads to a large energy barrier for H^+-ion diffusion. As a result, H^+-ion conductivity in LATP glass is negligible at room temperature. The results from this theoretical analysis agree well with the experimental observations and reveal
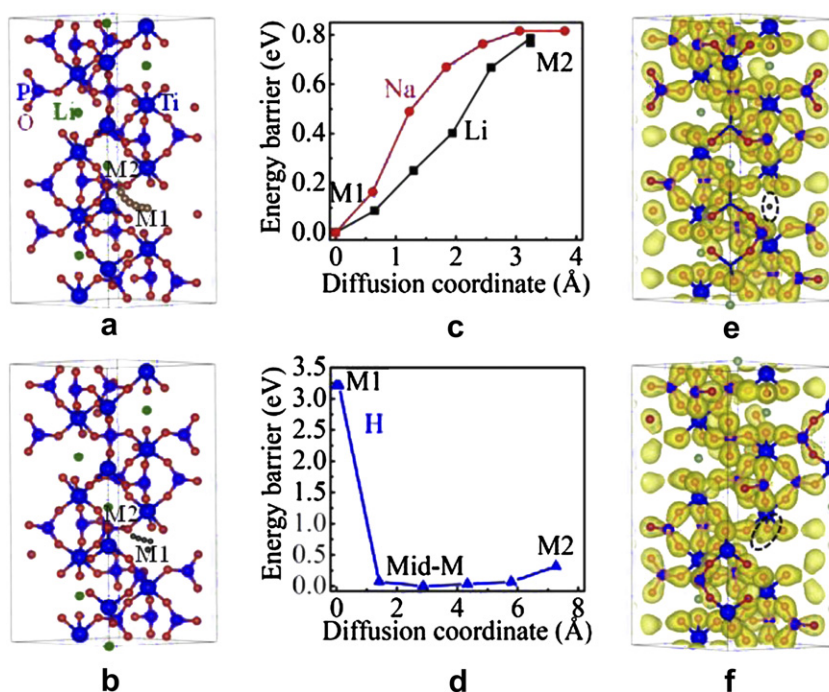
However, the H^+ adsorption at the LATP surface during the electrochemical process is not a simple physical adsorption process, and it may also involve the electrochemical reactions. The true nature of this adsorption still needs systematic investigations.

To fundamentally understand the transport properties of H^+, Li^+, and Na^+ ions in a LATP glass, we used density functional theory to calculate the ion (including H^+, Li^+, and Na^+) diffusion/transport barrier in NASICON-type LATP material. In a material with a NASICON structure, the Li^+ and Na^+ ions can occupy two positions in the conduction channels: the M1 site, which is coordinated by a trigonal antiprism of oxygen atoms, and the M2 site, which has a distorted eightfold coordination [24–27]. Long-range conduction of the ions in the NASICON structure is built up by ion diffusion between the M1 and M2 sites. Normally, Li^+ and Na^+ ions prefer to stay at M1 sites, and it will diffuse through M2 sites under higher

Fig. 6. Diffusion paths of (a) Li^+ (Na^+) and (b) H^+. Images (c) and (d) show the energy barriers for Li^+ (Na^+) and H^+ diffusion in NASICON glass. Images (e) and (f) show the charge density iso-surfaces of $LiTi_2(PO_4)_3$ with H^+ at the M1 and Mid-M sites, respectively.
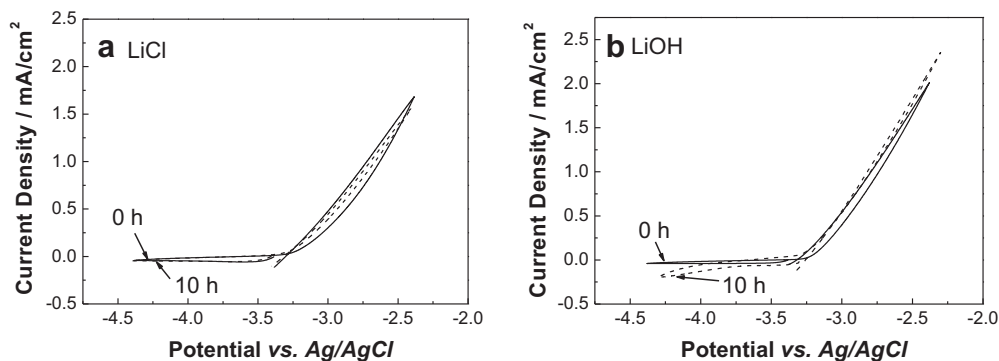
Fig. 7. CV curves of PLEs tested in 1 M HCl solution before and after soaking in LiCl electrolyte (a) and LiOH electrolyte (b). The OCP of the PLE in HCl solution is −3.36 V vs. Ag/AgCl.
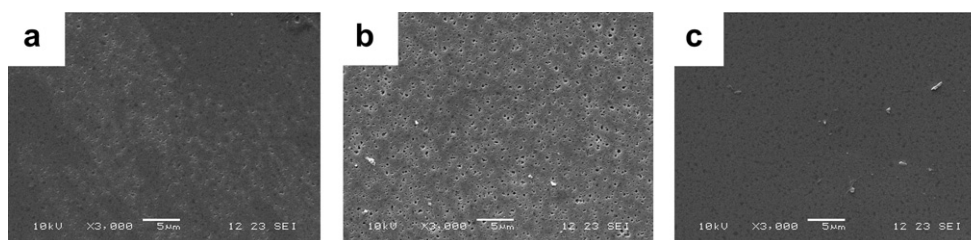

Fig. 8. Scanning electron microscopy images of fresh LATP glass (a), after storage for 10 h in LiOH electrolyte (b) and in LiCl electrolyte (c).

the fundamental mechanism that significantly limits H^+-ion diffusion in LATP glass.

It has been reported that surface adsorption depends, for the most part, on surface conditions such as surface area and surface active sites [29,30]. The surface conditions of LATP glass have been reported to change continuously when immersed in aqueous electrolytes [31,32]. In our work, we studied the effects of surface conditions on H^+-ion adsorption currents. Two typical aqueous electrolytes, 1-M LiCl and 1-M LiOH, were chosen to study the influence of LATP surface conditions on H^+-ion adsorption behavior. The PLE was soaked in either a LiCl or LiOH electrolyte for 10 h. The sets were sealed with a cap and para-film to avoid the CO_2 contamination from air. The H^+-ion adsorption behavior of the electrode was tested in 1-M HCl electrolyte before and after soaking in a LiCl or LiOH electrolyte.

Fig. 7(a) shows CV curves of the PLE before and after soaking in the 1-M LiCl electrolyte. Two similar cathodic I–V curves indicate that soaking for 10 h in LiCl solution does not significantly impact H^+-ion adsorption on the surface of LATP glass. However, after the electrode was soaked in 1-M LiOH electrolyte for the 10 h, a significantly higher H^+-adsorption current was observed when compared to the adsorption current observed for un-soaked samples (see Fig. 7(b)).

Fig. 8 compares the surface morphologies of LATP glass before and after soaking in LiCl or LiOH electrolytes. We observed a remarkable surface morphology change in the LATP glass soaked in the LiOH electrolyte (see Fig. 8(b)). This is a clear indication that the LATP glass can be easily corroded by the alkaline electrolyte. However, the LiCl electrolyte has little effect on the surface morphology of LATP glass (Fig. 8(c)). This result is consistent with results reported by Hasegawa and co-workers [31]. Obviously, the LATP glass is relatively stable in a neutral LiCl electrolyte. H^+-adsorption behavior on the LATP surface also is stable after soaking in the LiCl electrolyte. However, the surface morphology of the LATP glass changes significantly after soaking for a few hours in strong alkaline LiOH electrolytes, leading to large variations in H^+-adsorption on the surface of the LATP glass. As reported by

Thokchom and Kumar [33], the corrosion of the phosphate glass is probably caused by the hydrolysis of P–O–P bond in the phosphate material, especially in a strong basic or acid solution. This problem needs to be solved to attain long cycle life of LATP glass in Li–air batteries because large variations in pH are often observed during the deep charge/discharge cycling in these batteries.

Nevertheless, as a solid electrolyte that shows selective conduction of Li^+, Na^+ and H^+ ion, it is possible to use LATP glass as a selective electrode for the measurement of pLi or pNa in a similar way as those reported by *Baucke* [13], although further investigation on this material is still required for their industry applications.

4. Conclusions

We used several approaches to investigate the potential H^+ diffusion in LATP glass and interfacial reactions between H^+ ions and LATP glass. Our experimental and computational results reveal that H^+ ions cannot diffuse through LATP glass at room temperature. The apparent cathodic current observed in CV experiments and the increase of H^+-ion concentration in the testing chamber can be attributed to the H^+ ions adsorbing at the LATP glass surface. However, significant surface corrosion was found after the LATP glass was soaked in a strong alkaline electrolyte for extended time periods. This corrosion leads to increased H^+-ion adsorption on the LATP glass surface and an associated cathodic current during CV scans. Therefore, before Li–air batteries with aqueous electrolytes can be used for long-term applications, appropriate electrolytes must be developed to prevent LATP glass from corrosion.

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