

Reaction of $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ with water

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Recently, there has been an 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 [1–4]. One of the major requirements for the membrane is high Li-ion conductivity, which has resulted in renewed interest in the use of $\text{LiTi}_2(\text{PO}_4)_3$ (LTP) as a potential membrane [1–5]. In the above configuration, the chemical stability of the membrane with water is also a major concern. In this regard, the water stability of Al-doped LTP has been investigated by weight loss, X-ray diffraction, and ionic conductivity before and after immersion in distilled water [4, 6]. Cretin et al. [6] found approximately a 0.9% *weight* loss for a solid Al-doped LTP sample, with a relative density of ~95%, after immersion in distilled water for 100 h at room temperature. Hasegawa et al. [4] observed there was no significant difference in the X-ray diffraction patterns for an Al-doped LTP plate (relative density close to 100%) prepared by glass forming techniques after immersion in distilled water for 1 month [4]. Hasegawa et al. [4] also observed that the total resistance (sum of lattice and grain boundary resistances) of the Al-doped LTP plate increased by about a factor of 1.5 after 1 month in distilled water. The lattice resistance remained unchanged. They suggested that the change in total resistance was due to the formation of a new phase at the grain boundary [4]. Thokchom and Kumar [7] found that an Al-doped LTP membrane

prepared by glass forming techniques immersed in tap water for 65 days exhibited slight buckling.

Besides LTP, materials based on perovskite [8, 9] and garnet [10, 11] structures are also under consideration as possible membrane materials because of their high Li-ion conductivity. In particular, lithium lanthanum titanates, $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$, having a perovskite-type structure have exhibited very high bulk Li-ion conductivities [8, 12–14]. If lithium lanthanum titanates are to be used in the above configuration as possible membrane materials for Li-Air batteries, their water stability must be known. It is the purpose of this note to report on the water stability of $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ and compare the data to that for Al-doped LTP.

$\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ was chosen since this composition has one of the highest reported bulk Li-ion conductivities of the lithium lanthanum titanates [8, 9]. Stoichiometric amounts of La_2O_3 , TiO_2 (anatase), and Li_2CO_3 were mixed. The mixture was then heated in air at 10 °C degrees per min to 800 °C and held for 4 h before ramping at 10 °C per min to 1100 °C and held for 36 h before cooling to room temperature at 10 °C per min. The $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ powder was consolidated by hot pressing. The powders were hot-pressed in a graphite die lined with graphfoil, which was then heated to 1050 °C at which time a stress of 70 MPa was applied and held for a period of 1.5 h after which the load was removed and the sample cooled to room temperature. During the heating and cooling stages the furnace was flushed with flowing argon. For water stability testing, rectangular parallelepiped specimens of about 5 mm × 5 mm × 3 mm were cut from the hot-pressed disc using a low-speed diamond saw. The water stability of the $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ material was investigated by the structure (X-ray diffraction), weight, and ionic conductivity changes of hot-pressed $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ samples prior to and after being immersed

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in a sealed bottle of distilled water at room temperature for a period of 1 month. Prior to and after immersion, the $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ samples were heated at 60 °C for 24 h in air for X-ray diffraction, weight, and ionic conductivity measurements. In addition, the pH and Li-ion content of the distilled water solution were also measured. The bulk density of the hot-pressed samples was determined from the weight and physical dimensions and also by the Archimedes method using methanol as the immersion fluid. The relative density of the hot-pressed samples was $96 \pm 2\%$. AC measurements were undertaken to determine ionic conductivity. AC impedance was measured using a Solatron 1260 Impedance Analyzer in the frequency range 1– 10^6 Hz. Silver paste electrodes were applied to the top and bottom surfaces of the specimens prior to AC testing. The Li-ion content of the water solution before and 1 month after sample immersion was determined using inductively coupled plasma (ICP).

The color of the hot-pressed $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ samples was blue on the surface, indicating that reduction of Ti^{+4} to Ti^{+3} had occurred on the surface during hot-pressing as a result of the carbon foil and reducing atmosphere [15]. In order to convert the surface Ti^{+3} back to Ti^{+4} all hot-pressed samples were heated at 700 °C for 6 h under air. It was found that after this heat treatment all samples were colored white throughout the total thickness. All hot-pressed samples were given this additional annealing step prior to water stability testing.

Figure 1 shows the X-ray diffraction pattern of the $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ powder before (a) and after (b) immersion in distilled water for 1 month. The hot-pressed sample after immersion for 1 month time was ground into powder for X-ray diffraction. From Fig. 1a it can be seen that the starting $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ powder is single phase with the P4/mmm tetragonal space group indicative of some ordering of the La/Li in the A cation site of the ABO_3 perovskite structure. After immersion in distilled water, the X-ray diffraction pattern of $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ (Fig. 1b) does not change. Thus, we can conclude that there is no evidence of a water- $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ reaction from the X-ray diffraction data. This is in agreement with the results for Al-doped LTP [4]. The weight loss of the $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ material after 1 month in distilled water was approximately 0.15%. This is about 6 times lower than that for Al-doped LTP, even though the $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ sample was exposed to distilled water about 7 times longer than the Al-doped LTP sample [4]. This result suggests that $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ exhibits better water stability than Al-doped LTP.

The room temperature AC conductivity results for $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ before and after immersion in distilled water using Li-ion blocking silver electrodes are shown in the complex impedance plot in Fig. 2. From Fig 2, several important points are observed. First, it can be observed that the curves for the $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ material before and after

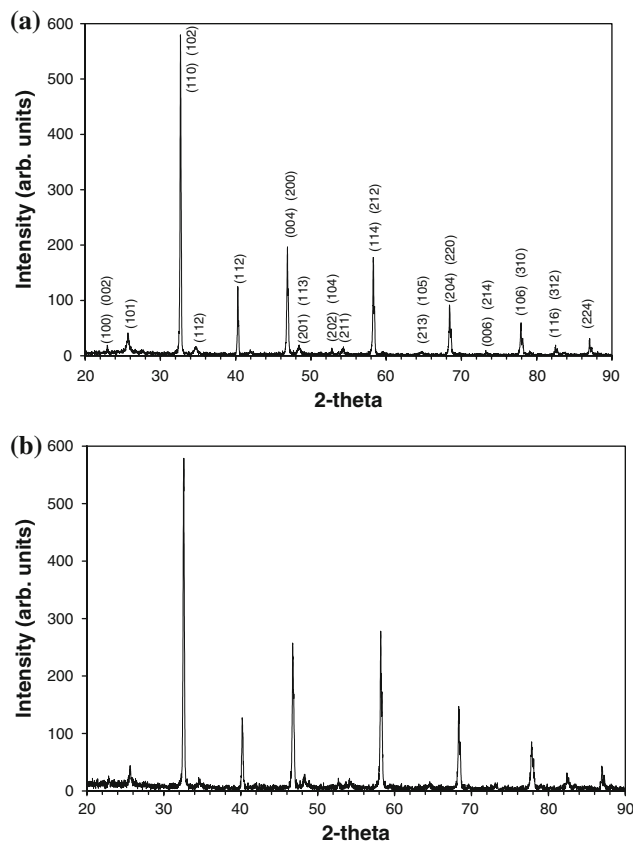


Fig. 1 X-ray diffraction pattern of $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ at room temperature before (a) and after immersion for 1 month (b) in distilled water

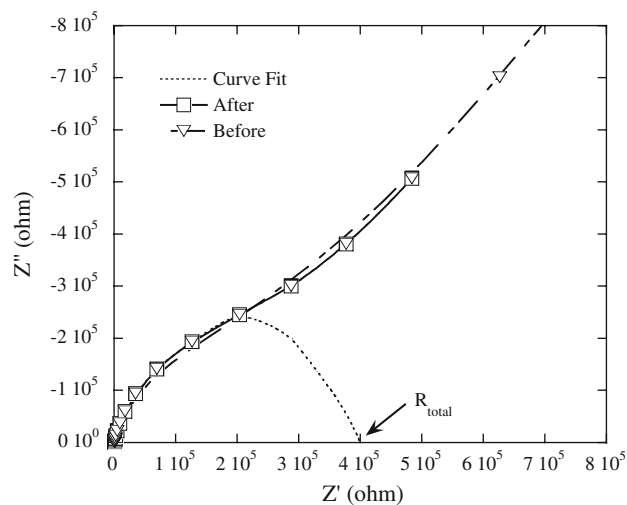


Fig. 2 Complex impedance plot of $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ at room temperature before and after immersion for 1 month in distilled water

water immersion superimpose on each other. Since the dimensions of both samples are the same, this means that they have the same conductivity values. The data for both samples separate into a high frequency region which contains a semicircle and a low-frequency region which

contains a spike. For this case, since we have Li blocking electrodes the shape of the curve represents a material that is predominately a Li-ion conductor with very low electronic conductivity [16, 17]. The low-frequency intercept (shown by the dotted line), R_{total} , of the extrapolated semicircle (the electrode contribution has been subtracted out) on the Z' -axis gives the total ionic resistance. Using this value and the sample dimensions yields a total ionic conductivity value of $\sim 6 \times 10^{-6}$ S/cm for the $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ material before and after water immersion. This value is in agreement with the total ionic conductivity of a lithium lanthanum titanate of similar composition and density [18]. Second, since the curves for the material before and after water immersion superimpose on each other, this suggests that there was no change in the total ionic conductivity after 1 month. This result can be compared to Al-doped LTP, where the total resistance increased approximately by a factor of about 1.5 after a month in distilled water [4]. Consequently, the ionic conductivity results reveal the superior water stability of $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ compared to Al-doped LTP.

The pH of the solution was almost constant (pH ~ 6.9) prior to and after sample immersion for a period of 1 month, implying little reaction between the distilled water and $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$. ICP analysis revealed that the Li concentration of the water solution for $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ was about 1.2×10^{-5} mol/L after 1 month. Cretin et al. [6] observed that the Li concentration for the Al-doped LTP material was 1.5×10^{-4} mol/L after 100 min. Since the starting Li concentration of the distilled water solution for the $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ and Al-doped LTP materials was similar, the observation that the final ICP Li content for the $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ water solution is about 12 times lower than that for Al-doped LTP water solution, even though the time was much longer (960 vs. ~ 1.5 h), reveals the enhanced water stability of $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ compared to Al-doped LTP.

The structure, weight loss, ionic conductivity, pH, and ICP results of this study reveal the excellent water stability of $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$. A comparison of the $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ results with Al-doped LTP reveals that $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ has the superior water stability. Hence, $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ is a potential membrane for Li-Air batteries where an aqueous electrolyte is used on the cathode side. Future studies will investigate the chemical stability of $\text{Li}_{0.33}\text{La}_{0.57}\text{TiO}_3$ in aqueous solutions of different pH.

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