Solvent-Free Composite PEO-Ceramic Fiber/Mat Electrolytes for Lithium Secondary Cells

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Solvent-free all-solid-state rechargeable lithium secondary cells have been studied extensively in recent years for cellular telephones, laptop computers, electric and hybrid vehicles, and aerospace applications. In a solid-state lithium cell, solid electrolytes serve both as an ionic conductor and separator. Therefore, they must meet requirements of high ionic conductivity, high lithium-ion transference number, and high electrochemical stability window, easy processability, and acceptable thermal and mechanical properties. Fibers based on poly(ethylene oxide) (PEO) form dimensionally stable films and show high chemical stability to reduction, but have low-temperature conductivities that are too low (10^-7 to 10^-5 S cm^-1) for most applications. Certain ceramics and glasses show much higher Li-ion conductivity. Lithium lanthanum titanate ceramic (La_{0.55}Li_{0.35}TiO_3) has the highest solid-state Li^+ conductivity reported to date (10^-3 S cm^-1) at room temperature. It has a conductivity of 1.8 x 10^-3 S cm^-1 at 50°C which is higher than that of typical PEO compositions at 25°C. Unfortunately, La_{0.55}Li_{0.35}TiO_3 ceramic cannot be directly used in lithium secondary cells because it is chemically unstable below 1.5 V vs. Li^+ due to Ti(V) to Ti(III) reduction. To enhance the chemical stability of La_{0.55}Li_{0.35}TiO_3 at low electrochemical potentials, thin layers of chemically stable PEO-salt complexes or ceramics such as LiPON have been placed between La_{0.55}Li_{0.35}TiO_3 plates and lithium metal or lithium-graphite anodes. The conductivities of these composite electrolytes can reach 10^-5 S cm^-1. However, their inflexibility and poor mechanical strength do not allow easy construction of suitable electrochemical secondary cells. Another possible design, that of filling PEO with nonconducting ceramic particles less than 1 μm, was observed by scanning electron microscopy (SEM) images using a Jeol JSM-6400 microscope equipped with a Noran 1-2 energy-dispersive spectrometer. A 15 kV beam was employed to generate the backscattered-electron images. Sintered La_{0.55}Li_{0.35}TiO_3 fibers of two different diameters (15 and 250 μm) were produced by Advanced Cerametrics, Inc. using its Viscount Suspension Spinning Process (VSSP) method. In the VSSP method, La_{0.55}Li_{0.35}TiO_3 powders were first dispersed in water to give a slurry, which was then mixed with viscose, i.e., cellulose in aqueous sodium hydroxide solution. The mixture was then pumped through a nozzle to form particulate La_{0.55}Li_{0.35}TiO_3-loaded cellulose (rayon) fibers. This was followed by sintering at 1325°C for 2 h. To fabricate La_{0.55}Li_{0.35}TiO_3 mats, cellulose fibers loaded with La_{0.55}Li_{0.35}TiO_3 particles were first woven into cloth-like mats, then sintered at 1350°C for 2 h.

The approach suggested here to achieve high ionic conductivity combined with chemical and mechanical stability is the use of La_{0.55}Li_{0.35}TiO_3 fibers and/or mats combined with PEO in which an additional very thin PEO layer is coated on the La_{0.55}Li_{0.35}TiO_3 surface. A parallel approach, that of filling PEO with nonconducting ceramic (or glass) fibers and mats to reinforce polymer electrolytes, has been reported. Incorporation of nonconducting ceramic fibers and mats into polymer electrolytes can enhance the mechanical properties of the electrolyte membranes, but decreases the ionic conductivity of the polymer electrolytes. However, La_{0.55}Li_{0.35}TiO_3 fiber-PEO electrolytes not only have good mechanical strength but also have high conductivity because the conducting fibers can penetrate the electrolyte film cross section to provide long-range Li^+ transfer channels. The conductivity of these composite electrolytes can be calculated from the measured conductivity of PEO and thevolume fraction of the ceramic fibers. The maximum transference number obtained was 0.7. The ceramic fibers in this composite electrolyte are coated by a very thin PEO layer, which is sufficient to provide good interfacial stability with lithium-ion and lithium-metal anodes.

Electrolyte preparation.—PEO polymer (Aldrich; Mn 600,000 Da) was dried under vacuum at 50°C for 24 h. Lithium bis(3-ethyl-3-dimethylamine nitrilo) imide [Li[N(SO_2)CF_2CF_3]]_2 (3M Company) and LiClO_4 (Aldrich) were dried at 120°C for 24 h. La_{0.55}Li_{0.35}TiO_3 (9.1 x 10^-4 S cm^-1) particles less than 1 μm were prepared from 50% Li_2CO_3, La_2O_3, and TiO_2 starting materials using Inaguma’s solid-state reaction method. Stoichiometric amounts of these powders were ground together in an agate mortar and calcined at 800°C for 4 h to eliminate CO_2. The heated powder was ballmilled with ethanol for 1 day, and heated again at 800°C for 2 h. The ballmilled powder was then sieved through a #325 mesh for fiber and mat preparation.

Experimental

La_{0.55}Li_{0.35}TiO_3 powders for filling PEO-LiClO_4 electrolytes were sintered at 1325°C for 2 h. The crystalline phases of La_{0.55}Li_{0.35}TiO_3 powders were identified by X-ray diffraction (XRD) analysis at room temperature using Cu Kα radiation. The 2θ range analyzed was 10-90°, and the scan rate was 2.0° per second. The particle size was observed by scanning electron microscopy (SEM) images using a Jeol JSM-6400 microscope equipped with a Noran 1-2 energy-dispersive spectrometer. A 15 kV beam was employed to generate the backscattered-electron images. Sintered La_{0.55}Li_{0.35}TiO_3 fibers of two different diameters (15 and 250 μm) were produced by Advanced Cerametrics, Inc. using its Viscount Suspension Spinning Process (VSSP) method. In the VSSP method, La_{0.55}Li_{0.35}TiO_3 powders were first dispersed in water to give a slurry, which was then mixed with viscose, i.e., cellulose in aqueous sodium hydroxide solution. The mixture was then pumped through a nozzle to form particulate La_{0.55}Li_{0.35}TiO_3-loaded cellulose (rayon) fibers. This was followed by sintering at 1325°C for 2 h. Fabricate La_{0.55}Li_{0.35}TiO_3 mats, cellulose fibers loaded with La_{0.55}Li_{0.35}TiO_3 particles were first woven into cloth-like mats, then sintered at 1350°C for 2 h. The approach suggested here to achieve high ionic conductivity combined with chemical and mechanical stability is the use of La_{0.55}Li_{0.35}TiO_3 fibers and/or mats combined with PEO in which an additional very thin PEO layer is coated on the La_{0.55}Li_{0.35}TiO_3 surface. A parallel approach, that of filling PEO with nonconducting ceramic (or glass) fibers and mats to reinforce polymer electrolytes, has been reported. Incorporation of nonconducting ceramic fibers and mats into polymer electrolytes can enhance the mechanical properties of the electrolyte membranes, but decreases the ionic conductivity of the polymer electrolytes. However, La_{0.55}Li_{0.35}TiO_3 fiber-PEO electrolytes not only have good mechanical strength but also have high conductivity because the conducting fibers can penetrate the electrolyte film cross section to provide long-range Li^+ transfer channels. The conductivity of these composite electrolytes can be calculated from the measured conductivity of PEO and the volume fraction of the ceramic fibers. The maximum transference number obtained was 0.7. The ceramic fibers in this composite electrolyte are coated by a very thin PEO layer, which is sufficient to provide good interfacial stability with lithium-ion and lithium-metal anodes.

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lithium salt in the same wt % ratio dissolved in acetonitrile into La$_{0.55}$Li$_{0.35}$TiO$_3$ mats, followed by rigorous drying as above.

Electrochemical measurements.—The ionic conductivity of the films was measured by electrochemical impedance spectroscopy (EIS) using symmetrical two-electrode cells sandwiching a film between two stainless steel plate electrodes. Spectra were obtained by sweeping from 65 kHz to 1 Hz with a Solartron FRA 1250 frequency analyzer and a Solartron model 1286 electrochemical interface. The high-frequency intercept of the Nyquist plot on the real axis gives the resistance $R$ of the electrolyte, from which the ionic conductivity is calculated. Li$^+$ transference number ($t_{\text{Li}^+}$) measurements were conducted on symmetrical lithium/composite electrolyte/lithium cells by using the method of Bruce and Vincent. 11

The stability of the composite electrolyte-lithium electrode interface was investigated by monitoring the time dependence of the impedance of symmetrical Li/composite electrolyte/Li cells under open-circuit conditions. This impedance measurement was obtained by sweeping from 65 kHz to 0.01 Hz using the same equipment as that for the ionic conductivity measurements.

Results and Discussion

Preparation of La$_{2/3}$-$\text{Li}_x\text{TiO}_3$ particles, fibers, and mats.— Figure 1 shows the XRD patterns of La$_{0.55}$Li$_{0.35}$TiO$_3$ powders calcined at 800°C and sintered at 1325°C. The powders calcined at 800°C consist only of a mixture of La$_2$O$_3$, Li$_2$O, and TiO$_2$. However, the sintered powders were La$_{0.55}$Li$_{0.35}$TiO$_3$, which has a cubic perovskite-type structure. The XRD patterns of the sintered La$_{0.55}$Li$_{0.35}$TiO$_3$ powders are in agreement with the previously reported XRD data of a ceramic with a similar composition. 12

La$_{0.55}$Li$_{0.35}$TiO$_3$ fibers and mats were made from ballmilled La$_{0.55}$Li$_{0.35}$TiO$_3$ particles using the VSSP method. Figure 2 shows SEM images of the ballmilled La$_{0.55}$Li$_{0.35}$TiO$_3$ particles used to prepare fibers and mats. The particle size of La$_{0.55}$Li$_{0.35}$TiO$_3$ was less than 1 μm after ballmilling for 1 day. Some La$_{0.55}$Li$_{0.35}$TiO$_3$ particles were agglomerated to form large porous particles of 2-3 μm diam. La$_{0.55}$Li$_{0.35}$TiO$_3$-loaded cellulose fibers (green fibers) of 15 and 250 μm diam were successfully made from ballmilled La$_{0.55}$Li$_{0.35}$TiO$_3$ particles. Figure 3 shows a spool of green La$_{0.55}$Li$_{0.35}$TiO$_3$ fiber of 15 μm diam, which was woven into a mat (Fig. 4), then sintered at 1325°C for 2 h. Figure 5 shows sintered La$_{0.55}$Li$_{0.35}$TiO$_3$ 15 μm diam fibers and sintered woven La$_{0.55}$Li$_{0.35}$TiO$_3$ mats.

Figure 1. XRD patterns of La$_{0.55}$Li$_{0.35}$TiO$_3$ powders calcined at 800°C and sintered at 1325°C.

Figure 2. SEM images of the La$_{0.55}$Li$_{0.35}$TiO$_3$ particles prepared by solid-state reaction.

Figure 3. A spool of green La$_{0.55}$Li$_{0.35}$TiO$_3$ fiber of 15 μm diam.

Figure 4. Woven mats made from green La$_{0.55}$Li$_{0.35}$TiO$_3$ fibers of 15 μm diam.
Ionic conductivity of fiber-PEO electrolytes.—Perovskite oxides of ABO$_3$ type such as La$_{0.67}$Li$_{0.33}$TiO$_3$ have exceptional ionic conductivity, first reported by Inaguma. However, ceramic membranes formed from these materials are brittle, making them difficult to use in secondary cells. The easiest way to give these materials flexibility is to load particles of ceramic into PEO-salt complexes to form composite polymer electrolytes, which have higher conductivity than the host PEO electrolytes. In these conducting particle-PEO composite electrolytes, ceramic particles are homogeneously dispersed in the PEO matrix, and hence are separated by relatively thick polymer layers. The poorly conducting contacts between ceramic particles prevent much improvement of conductivity over that of the PEO host. However, conducting ceramic fibers can bridge the gap in the electrolyte film cross section, and hence provide long-range Li$^+$ transfer channels. Figure 6 compares the ionic conductivities of electrolytes with 20 wt % La$_{0.55}$Li$_{0.35}$TiO$_3$ particles and 20 wt % La$_{0.55}$Li$_{0.35}$TiO$_3$, 250 μm diam fibers in PEO-LiN(SO$_2$CF$_2$CF$_3$)$_2$. The fiber-PEO electrolyte has higher conductivity than the particle-PEO electrolyte over the temperature range studied. The room-temperature conductivity of 20 wt % La$_{0.55}$Li$_{0.35}$TiO$_3$ fiber-PEO-LiN(SO$_2$CF$_2$CF$_3$)$_2$ was 5.0 × 10$^{-4}$ S·cm$^{-1}$.

Figure 7 shows the temperature dependence of ionic conductivity for 50 wt % La$_{0.55}$Li$_{0.35}$TiO$_3$ fiber-PEO-LiClO$_4$ electrolytes with different fiber diameters. Compared to thick fiber-PEO electrolytes, those with thin fibers have a higher area-to-volume ratio in the electrolyte film, giving higher conductivity over the whole temperature range. Fiber diameter therefore plays an important role in determining the ionic conductivity of fiber-PEO composite electrolytes, as does the choice of lithium salt. Figure 8 shows the temperature dependence of ionic conductivity for 250 μm diam La$_{0.55}$Li$_{0.35}$TiO$_3$ fiber-PEO-LiClO$_4$ and -PEO-LiN(SO$_2$CF$_2$CF$_3$)$_2$ electrolytes. Because the conductivity of La$_{0.55}$Li$_{0.35}$TiO$_3$ fiber is not influenced by the presence of the lithium salt, any changes in ionic conductivity must occur in the PEO matrix. LiN(SO$_2$CF$_2$CF$_3$)$_2$ has large anions which can influence the PEO polymer chain crystallization process, promoting amorphous regions with increased ionic conductivity. Therefore, the PEO matrix conductivity still plays an important role in the overall conductivity properties of these composite electrolytes, although the conducting fibers dominate in Li$^+$ transfer.

One disadvantage of PEO-based polymer electrolytes is that polymer chain thermal motion can cause the amorphous PEO phase to slowly recrystallize at room temperature, which results in a loss of ionic conductivity during storage. Figure 9 shows the change in the relative conductivity ($\sigma/\sigma_0$) for PEO-LiN(SO$_2$CF$_2$CF$_3$)$_2$ and 20 wt % La$_{0.55}$Li$_{0.35}$TiO$_3$ fiber (250 μm)-PEO-LiN(SO$_2$CF$_2$CF$_3$)$_2$ electrolytes over a 35 day period at 25°C. The conductivity of La$_{0.55}$Li$_{0.35}$TiO$_3$ fiber, which penetrates the electrolyte cross section, does not change much during storage. At the same time, the ceramic fibers can also stabilize the conductivity of the PEO matrix by hindering its recrystallization. Therefore, the conductivity loss of La$_{0.55}$Li$_{0.35}$TiO$_3$ fiber-PEO composite electrolyte is less than that of the host polymer electrolyte.

Ionic conductivity and Li$^+$ transference number of mat-PEO electrolytes.—Fiber-PEO composite electrolytes have a higher conductivity than particle-PEO electrolytes because La$_{0.55}$Li$_{0.35}$TiO$_3$ fibers can provide long-range Li$^+$ transfer channels through the electrolyte film. However, most fibers are parallel to the film plane, hence, only some of the fibers can penetrate the electrolyte completely. Therefore, PEO host conductivity still plays an important role in the overall conductivity of fiber-PEO composite electrolytes, as is shown in Fig. 8. However, when the conducting fibers are woven into mats, they can penetrate the film cross section more readily. Figure 10 compares the ionic conductivities of 50 wt %
La$_{0.55}$Li$_{0.35}$TiO$_3$ fiber-PEO-LiClO$_4$ and 70 wt % La$_{0.55}$Li$_{0.35}$TiO$_3$ mat-PEO-LiClO$_4$ composite electrolytes. Fiber-PEO composite electrolytes with higher than 50 wt % fiber content are easily torn because the fibers are in parallel and the PEO matrix is not strong enough for bonding. The fiber content (70 wt %) of La$_{0.55}$Li$_{0.35}$TiO$_3$ mat-PEO-LiClO$_4$ electrolytes was obtained by weighing the La$_{0.55}$Li$_{0.35}$TiO$_3$ mat and PEO-LiClO$_4$ used. From Fig. 10, it is clearly seen that the mat-PEO composite electrolyte has higher conductivity than the fiber-PEO electrolyte over the whole temperature range studied because of its higher fiber content combined with its regular weave pattern.

The addition of conducting particles only slightly improves the Li$^+$ transference number. However, the Li$^+$ transference number of La$_{0.55}$Li$_{0.35}$TiO$_3$ mat-PEO-LiClO$_4$ composite electrolyte was determined to be about 0.7, much higher than the highest number ($t_{Li^+} = 0.39$) given by La$_{0.55}$Li$_{0.35}$TiO$_3$ particle-filled PEO electrolytes. The high Li$^+$ transference number for the La$_{0.55}$Li$_{0.35}$TiO$_3$ mat-PEO-LiClO$_4$ composite electrolyte was attributed to the large amount of Li$^+$-conducting ($t_{Li^+} = 1.0$) La$_{0.55}$Li$_{0.35}$TiO$_3$ mat in the composite electrolytes.

Interfacial stability with lithium electrode.—La$_{0.55}$Li$_{0.35}$TiO$_3$ ceramic reacts with lithium metal, reducing the tetravalent titanium ions, and producing an electronic or electronic-ionic mixed conductor. As a result, it is very important to prevent the direct contact of ceramic and lithium anodes. In fiber-PEO and mat-PEO composite electrolytes, the conducting ceramic is coated with a very thin PEO-salt layer, which separates the ceramic and lithium electrode. A 20 wt % La$_{0.55}$Li$_{0.35}$TiO$_3$ fiber-PEO-LiN(SO$_2$CF$_2$CF$_3$)$_2$ was sandwiched between two lithium electrodes in a glove box. The color of the sample did not change with time, indicating that no reaction between La$_{0.55}$Li$_{0.35}$TiO$_3$ ceramic and lithium metal occurred, because the color changes from ivory to blue-black on reduction.$^1$

Any reduction of tetravalent titanium ions starts at the electrolyte-electrode interface. The interfacial resistance between 20 wt % La$_{0.55}$Li$_{0.35}$TiO$_3$ fiber-PEO-LiN(SO$_2$CF$_2$CF$_3$)$_2$ composite electrolyte and lithium electrode was monitored as a function of time, as shown in Fig. 11. The time dependence of the interfacial resistance for PEO-LiN(SO$_2$CF$_2$CF$_3$)$_2$ polymer electrolyte is also shown. The interfacial resistance of the latter electrolyte increases markedly at first, then increases irregularly. The initial increase indicates formation of a passivation layer, and the subsequent irregular increase shows that its structure is unstable. The addition of La$_{0.55}$Li$_{0.35}$TiO$_3$ fiber should make the interfacial resistance more unstable if reaction is occurring. However, Fig. 11 shows that La$_{0.55}$Li$_{0.35}$TiO$_3$ fiber stabilizes the interfacial resistance, indicating no interfacial reaction. This interfacial stabilization is attributed to the ability of the La$_{0.55}$Li$_{0.35}$TiO$_3$ fiber surface to scavenge traces of residual impurities in a similar way to added nonconducting ceramic particles.$^{13,14}$

Conclusions

High-ionic-conducting La$_{0.55}$Li$_{0.35}$TiO$_3$ fibers and mats were successfully prepared using the VSSP method. La$_{0.55}$Li$_{0.35}$TiO$_3$ fibers in fiber-PEO and mat-PEO composite electrolytes can penetrate the electrolyte film, and hence provide long-range Li$^+$ transfer channels. La$_{0.55}$Li$_{0.35}$TiO$_3$ mat-PEO composite electrolyte has higher conductivity than fiber-PEO electrolyte because of the woven pattern and higher fiber content. The fiber diameter and the salt type also play an important role in the overall conductivity properties of composite electrolytes.

The reaction between La$_{0.55}$Li$_{0.35}$TiO$_3$ ceramic and lithium anodes is also prevented by the thin PEO-salt layer on the fiber surface. Therefore, these composite electrolytes have good interfacial stability with lithium metal and lithium-ion anodes.

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