

Solvent-free composite PEO-ceramic-fiber-mat electrolytes for lithium secondary cells

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Abstract

Solvent-free composite polyethylene oxide (PEO)-ceramic-fiber or -mat electrolytes with high ionic conductivity and good interfacial stability have been developed using high-ionic-conductivity $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ fibers and mats. The conducting ceramic fibers can penetrate the cross-section of the electrolyte film to provide long-range lithium ion transfer channels, and giving composite electrolytes with high conductivity. In this work, a maximum room-temperature conductivity of $5.0 \times 10^{-4} \text{ S cm}^{-1}$ was achieved for 20 wt % $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ fiber in a PEO-LiN(SO₂CF₂CF₃)₂ mixture containing 12.5 wt % Li⁺ in PEO. 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.

1. Introduction

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. Electrolytes based on polyethylene oxide (PEO) form dimensionally stable films and show high chemical stability to reduction, but have room-temperature conductivities which are too low (10^{-7} to $10^{-8} \text{ S-cm}^{-1}$) for most applications. Lithium lanthanum titanate ceramic ($\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$) has the highest solid-state Li⁺ conductivity reported to date ($\sim 10^{-3} \text{ S-cm}^{-1}$) at room temperature [1-4]. Indeed, its conductivity of $1.8 \times 10^{-5} \text{ S-cm}^{-1}$ at -50°C is higher than that of typical PEO compositions at 25°C . Unfortunately, $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ ceramic can not be directly used in lithium secondary cells because it is chemically unstable below 1.5 V vs. Li⁰ due to Ti (IV) to Ti (III) reduction [1, 3]. To enhance the chemical stability of $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ at low electrochemical potentials, thin layers of chemically-stable PEO-salt complexes or ceramics such as LiPON have been placed between $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ plates and lithium metal or lithiated graphite anodes [4, 5]. The conductivities of these composite electrolytes can reach $10^{-4} \text{ S-cm}^{-1}$. However, their inflexibility and poor mechanical strength do not allow the easy construction of suitable electrochemical secondary cells. Another possible design puts high-conductivity ceramic particles into a PEO-salt complex to form a composite solid polymer electrolyte [6]. However, poorly conducting interparticle contact results in little improvement in conductivity over that of PEO alone.

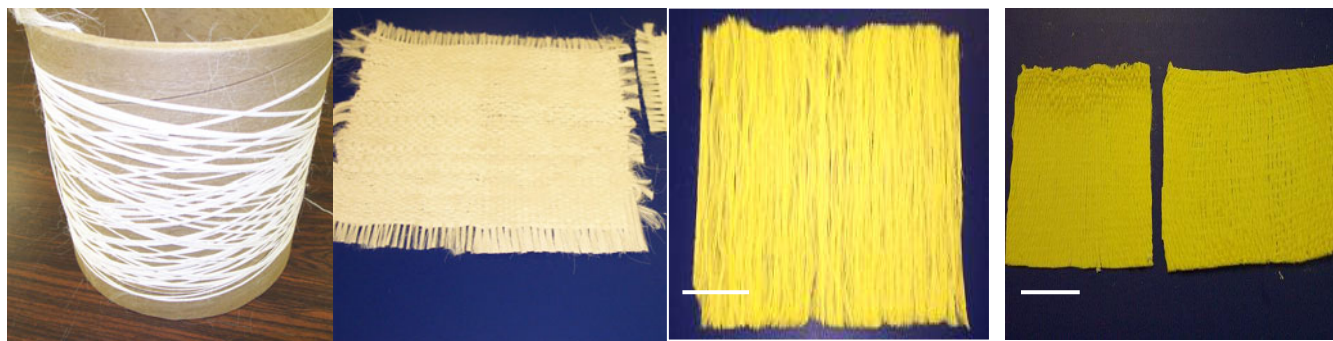
The approach suggested here to achieve high ionic conductivity combined with chemical and mechanical stability is the use of $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ fibers and/or mats combined with PEO in which an additional very thin PEO layer is coated on the $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ surface. $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ fiber-PEO electrolytes not only have good mechanical strength but also high conductivity because the conducting fibers can penetrate the electrolyte film cross-section to provide long-range Li⁺ transfer channels. The conducting fibers in $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ mat-PEO electrolytes have a similar function, but their woven pattern provides better bridging.

2. Experimental

PEO polymer (Aldrich; molecular weight 600,000 Da) was dried under vacuum at 50°C for 24 h. Lithium bis(perfluoroethylsulfonyl) imide ($\text{LiN}(\text{SO}_2\text{CF}_2\text{CF}_3)_2$; 3M Company) and LiClO_4 (Aldrich) were dried at 120°C for 24 h. Sintered $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ fibers of two different diameters (15 and 250 μm) were produced by Advanced Cerametrics, Inc. using its Viscous Suspension Spinning Process (VSSP) method [7]. $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ fiber-PEO composite electrolytes were prepared from acetonitrile dispersions of weighed quantities of fiber, lithium salt and PEO to give 12.5 wt % Li^+ in the PEO matrix. These were ultrasonically vibrated for 8.0 h, cast onto PTFE films and dried in air for 24 h, then vacuum dried at 25°C, followed by 80°C, each for 24 h. $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ mat-PEO composite electrolytes were prepared by dropping a fresh solution of PEO and lithium salt in the same wt % ratio dissolved in acetonitrile into $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ mats, followed by rigorous drying as above. 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 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 ionic conductivity measurement.

3. Results and Discussion

$\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ -loaded cellulose fibers (green fibers) with a diameter of 15 μm and 250 μm were successfully made from ball-milled $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ particles. Figure 1a shows a spool of green $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ fiber with a diameter of 15 μm , which were woven into a mat (Figure 1b), then sintered at 1325°C for 2 h. Figure 1c and d shows sintered $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ 15



(a)

(b)

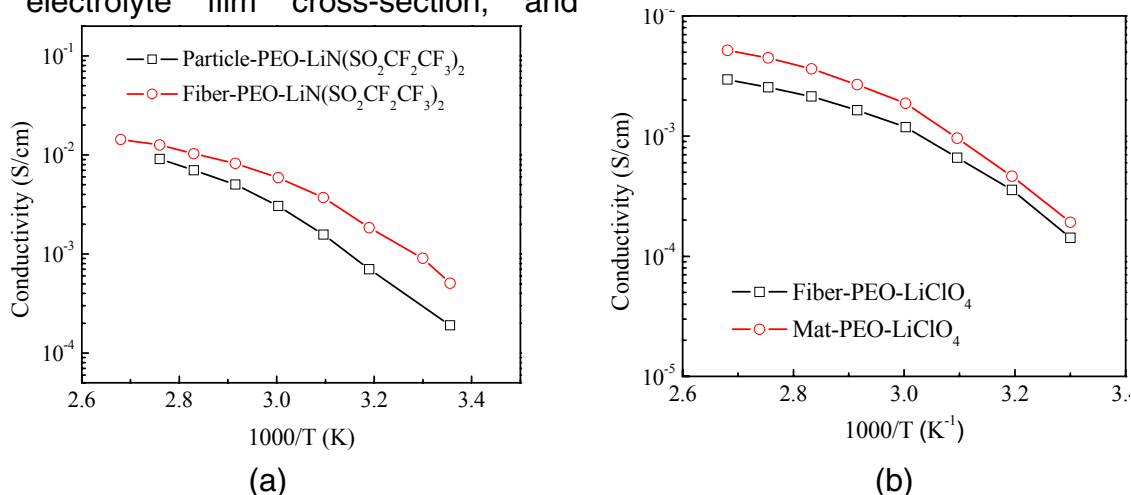
(c)

(d)

μm diameter fibers and sintered woven $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ mats, respectively.

Fig.1.(a) A spool of green $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ fiber with a diameter of 15 μm , (b) Woven mats made from green $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ fibers with a diameter of 15 μm , (c) Sintered $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ fibers and (d) Sintered $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ mats.

Figure 2a compares the ionic conductivities of electrolytes with 20 wt % $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ particles and 20 wt % $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ 250 μm diameter fibers in $\text{PEO-LiN}(\text{SO}_2\text{CF}_2\text{CF}_3)_2$. The fiber-PEO electrolyte has higher conductivity than particle-PEO electrolyte over the temperature range studied. The room-temperature conductivity of 20 wt % $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ fiber-PEO- $\text{LiN}(\text{SO}_2\text{CF}_2\text{CF}_3)_2$ electrolyte was $5.0 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$. The high Li ion conductivity of ceramic fiber-PEO composite is because that conducting ceramic fibers can bridge the gap in the electrolyte film cross-section, and



hence provide long-range Li^+ transfer channels.

Figure 2. (a) Arrhenius plots for 20 wt % $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ particle-PEO- $\text{LiN}(\text{SO}_2\text{CF}_2\text{CF}_3)_2$ and 20 wt % $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ fiber (250 μm)-PEO- $\text{LiN}(\text{SO}_2\text{CF}_2\text{CF}_3)_2$ composite electrolytes, (b) Arrhenius plots for 50 wt % $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ fiber-PEO- LiClO_4 and 70 wt % $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ mat-PEO- LiClO_4 composite electrolytes.

Figure 2b compares the ionic conductivities of 50 wt % $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ fiber-PEO- LiClO_4 and 70 wt % $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ mat-PEO- LiClO_4 composite electrolytes. Fiber-PEO composite electrolytes with higher than 50 wt % fiber content can be easily torn because the fibers are in parallel and the PEO matrix is not strong enough for bonding. The fiber content (70 wt %) of $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ mat-PEO- LiClO_4 electrolytes was obtained by weighing the $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ mat and PEO- LiClO_4 used. From Figure 2b, it is clearly seen 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. Addition of conducting particles only slightly improves the Li^+ transference number [6]. However, the Li^+ transference number of $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ mat-PEO- LiClO_4 composite electrolyte was determined to be about 0.7, much higher than the highest number ($t_{\text{Li}^+} = 0.39$) given by $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ particle-filled PEO electrolytes [6]. The high Li^+ transference number for $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ mat-PEO- LiClO_4 composite electrolyte was attributed to the large amount of Li^+ -conducting ($t_{\text{Li}^+} = 1.0$) $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ mat in the composite electrolytes.

$\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ ceramic reacts with lithium metal, reducing the tetravalent titanium ions, and producing an electronic or electronic-ionic mixed conductor [1]. 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 % $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ fiber-PEO- $\text{LiN}(\text{SO}_2\text{CF}_2\text{CF}_3)_2$ was sandwiched between two lithium electrodes in glove box. It is found that

the color of the sample did not change with time, indicating that no reaction between $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ ceramic and lithium metal, since color changes from ivory to blue-black on reduction [1].

Any reduction of tetravalent titanium ions will start at the electrolyte-electrode interface. The interfacial resistance between 20 wt % $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ fiber-PEO-LiN(SO₂CF₂CF₃)₂ composite electrolyte and lithium electrode was monitored as a function of time. The time dependence of the interfacial resistance for PEO-LiN(SO₂CF₂CF₃)₂ polymer electrolyte is also shown. It is seen that 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 $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ fiber should make the interfacial resistance more unstable if reaction is occurring. However, the result shows that $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ fiber in fact *stabilizes* the interfacial resistance, indicating no interfacial reaction. This interfacial stabilization is attributed to the ability of the $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ fiber surface to scavenge traces of residual impurities in a similar way to added non-conducting ceramic particles [8,9].

Conclusions

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