

**Solvent-free Composite PEO-ceramic-fiber-mat Electrolytes for Li-ion Batteries**

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Solvent-free composite polyethylene oxide (PEO)-ceramic-fiber or -mat electrolytes with high ionic conductivity and good interfacial stability were developed using high-ionic conducting  $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$  fibers and mats. The conducting ceramic fibers can penetrate the electrolyte film cross-section to provide long-range lithium ion transfer channels, and hence endow the composite electrolytes with high conductivity. A maximum room-temperature conductivity of  $5.0 \times 10^{-4} \text{ S cm}^{-1}$  is achieved for 20 wt %  $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$  fiber-PEO- $\text{LiN}(\text{SO}_2\text{CF}_2\text{CF}_3)_2$  in this study. The ceramic fibers in composite electrolytes are coated by a very thin PEO layer, which provides good interfacial stability with lithium electrode..

**1. Introduction**

lithium lanthanum titanate ceramic ( $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ ) has the highest solid-state  $\text{Li}^+$  conductivity reported to date ( $\sim 10^{-3} \text{ S cm}^{-1}$ ) at room temperature. Its conductivity at temperature of  $-50^\circ\text{C}$  ( $1.8 \times 10^{-5} \text{ S cm}^{-1}$ ) is even higher than the conductivity of PEO at room temperature. Unfortunately,  $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$  ceramic can not be directly used in lithium battery because it is chemically unstable below 1.5 V (vs.  $\text{Li}^0$ ) due to the reduction reaction from Ti(IV) to Ti(III) [1, 3]. To enhance the low-potential chemical stability of  $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$  ceramic, a thin layer of chemical stable LiPON or PEO-salt complexes were placed between the  $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$  ceramic plates and lithium metal (or lithiated graphite). The conductivities of these composite electrolytes can reach to  $10^{-4} \text{ S cm}^{-1}$ . However, their inflexibility and poor mechanical strength do not allow an easy construction of a unit battery cell configuration

The approach suggested here to achieve high conductivities, chemical and mechanical stability is the formulation of  $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$  fiber-PEO and  $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$  mat-PEO composite solid electrolytes in which an additional very thin PEO layer are 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 have high conductivity as well because the conducting fibers can penetrate the electrolyte film cross-section to provide long-range  $\text{Li}^+$  transfer channels. The conducting fibers in  $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$  mat-PEO electrolytes have similar function, but better penetration because of the woven pattern.

**. Results and Discussion**

*Preparation of  $\text{La}_{2/3-x}\text{Li}_x\text{TiO}_3$  particles, fibers and mats*

The  $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$ -loaded cellulose fibers (green fibers) with a diameter of 15  $\mu\text{m}$  and 250 $\mu\text{m}$  were successfully made from ball-milled  $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$  particles. Figure 1 shows a spool of green  $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$  fiber with a

diameter of 15  $\mu\text{m}$ . The green fibers with a diameter of 15 $\mu\text{m}$  were woven into a mat (Figure 2). Fibers with diameters of 15 $\mu\text{m}$  and 250 $\mu\text{m}$  were then sintered at 1325  $^\circ\text{C}$  for 2h, and woven mats made from 15 $\mu\text{m}$  green fiber were also sintered at 1350  $^\circ\text{C}$  for 2 h. Figure 3 shows sintered  $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$  fibers with a diameter of 15  $\mu\text{m}$  and the sintered woven  $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$  mats.

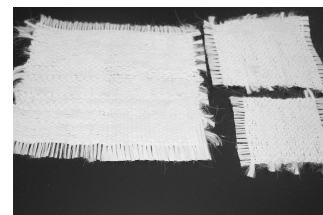


Figure 1. A spool of green  $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$  fiber with a diameter of 15  $\mu\text{m}$

Figure 2. Woven mats made from green  $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$  fibers

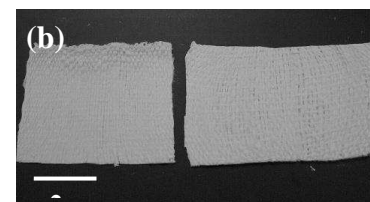
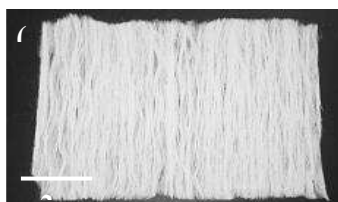


Figure 3. Sintered  $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$  fibers and mats

*Ionic Conductivity and  $\text{Li}^+$  transference number of mat-PEO Electrolytes*

When the conducting fibers are woven into mats,  $\text{Li}^+$  ion can penetrate the film cross-section easier. Figure 4 compares the ionic conductivities of 50 wt %  $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$  fiber-PEO- $\text{LiClO}_4$  and 70 wt %  $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$  mat-PEO- $\text{LiClO}_4$  composite electrolytes. Fiber-PEO composite electrolytes with higher than 50 wt % fiber content can be easily torn into pieces because the fibers are arrayed in parallel and PEO matrix are not strong enough to bond them together.

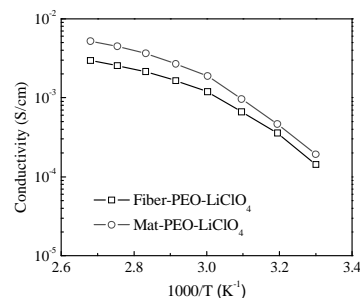


Figure 4. Arrhenius plots for 50 wt %  $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$  fiber-PEO- $\text{LiClO}_4$  and 70 wt %  $\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$  mat-PEO- $\text{LiClO}_4$  composite electrolytes.

**Conclusions**

$\text{La}_{0.55}\text{Li}_{0.35}\text{TiO}_3$  mat-PEO composite electrolyte has higher conductivity than fiber-PEO electrolyte because of the woven pattern and higher fiber content. Fiber diameter and salt type also play an important role in the overall conductivity properties of composite electrolytes.