



## Facile and scalable fabrication of polymer-ceramic composite electrolyte with high ceramic loadings



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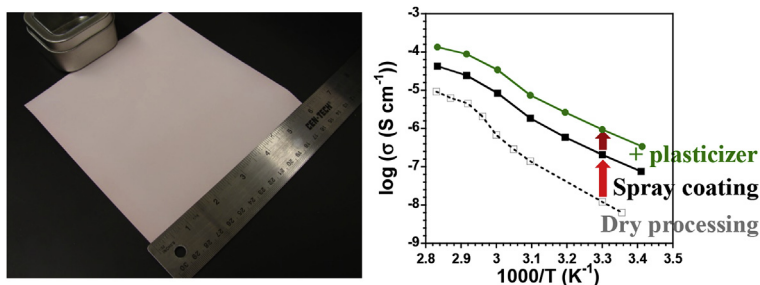
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### HIGHLIGHTS

- Composite electrolytes with 60 vol% ceramic are prepared by spray coating.
- Spray-coated membranes have 10 times higher conductivity than other methods.
- A  $\text{Li}^+$  transference number of 0.79 is discovered for the composite membrane.
- Symmetrical cell Li/composite electrolyte/Li can cycle for 85 h at 30 °C.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Keywords:

Composite electrolyte  
Aqueous processing  
Spray coating  
Lithium ion conductivity  
Solid state lithium battery

### ABSTRACT

Solid state electrolytes are a promising alternative to flammable liquid electrolytes for high-energy lithium battery applications. In this work polymer-ceramic composite electrolyte membrane with high ceramic loading (greater than 60 vol%) is fabricated using a model polymer electrolyte poly(ethylene oxide) + lithium trifluoromethane sulfonate and a lithium-conducting ceramic powder. The effects of processing methods, choice of plasticizer and varying composition on ionic conductivity of the composite electrolyte are thoroughly investigated. The physical, structural and thermal properties of the composites are exhaustively characterized. We demonstrate that aqueous spray coating followed by hot pressing is a scalable and inexpensive technique to obtain composite membranes that are amazingly dense and uniform. The ionic conductivity of composites fabricated using this protocol is at least one order of magnitude higher than those made by dry milling and solution casting. The introduction of tetraethylene glycol dimethyl ether further increases the ionic conductivity. The composite electrolyte's interfacial compatibility with metallic lithium and good cyclability is verified by constructing lithium symmetrical cells. A remarkable  $\text{Li}^+$  transference number of 0.79 is discovered for the composite electrolyte.

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## 1. Introduction

Solid electrolytes are a promising alternative to flammable liquid electrolytes for high-energy lithium battery applications. There are two important classes of solid electrolytes, polymer electrolytes and ceramic electrolytes. Polymer electrolytes are usually stable against metallic lithium [1,2]. Their mechanical flexibility provides resistance to fracture and accommodates volume changes during cycling. They also form relatively good adhesion to electrodes. Low room temperature ionic conductivity ( $< 10^{-5} \text{ S cm}^{-1}$ ) and low shear modulus ( $< 1 \text{ GPa}$ ) are major disadvantages of polymer electrolytes. Ceramic electrolytes have the mechanical rigidity to withstand lithium dendrite growth with ionic conductivity slightly lower than liquid electrolytes. High grain-boundary impedance and brittleness are major disadvantages of ceramic electrolytes. Many ceramic electrolytes are not stable against metallic lithium. Both classes of electrolytes attracted much attention due to their intrinsic safety compared to organic liquid electrolytes.

Poly(ethylene oxide) (PEO) is the most widely studied base polymer to form polymer electrolytes. PEO has a linear chain architecture containing ether oxygen groups. When a lithium salt is dissolved in PEO,  $\text{Li}^+$  ions coordinate with ether oxygens and  $\text{Li}^+$  ion movement is promoted by the segmental motion of PEO chains. However, PEO crystallizes below its melting temperature ( $\sim 65^\circ\text{C}$ ). This lowers the ionic conductivity by several orders of magnitude. Ionic conductivity is also affected by the total quantity and mobility of available charge carriers. One way to enhance the ionic conductivity is to introduce plasticizers or co-solvents that can enhance the number of available charge carriers and improve their mobility in the electrolyte. Exposing polymer electrolytes to vapors of dimethylformamide, dimethyl sulfoxide, water, and methanol has shown an increase in ionic conductivity [3]. However, the stability of the above solvents against metallic lithium makes them not suitable for batteries. Small molecules like bis(2-methoxyethyl) ether (diglyme), tetraethylene glycol dimethyl ether (TEGDME) and propylene carbonate (PC) have been used in polymer electrolytes for battery applications. Generally, adding plasticizers decreases the modulus of polymer electrolytes.

To improve the properties of polymer electrolytes, composites incorporating non-conducting filler materials like  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{SiO}_2$  and  $\text{ZrO}_2$  [4–9] have been fabricated. In these composites, the optimal filler loading for enhanced conductivity is between 10 and 15 vol%. Increase in filler loading beyond this value decreases the overall conductivity of the electrolyte due to the dilution effect [10]. Addition of ceramic fillers may also improve the mechanical strength of the electrolyte. Kalnaus [11] developed stability criteria for the composite electrolyte material based on the assumption that the shear modulus of the electrolyte needs to be approximately twice the shear modulus of lithium metal when the effective Poisson's ratio is 0.33. Accordingly, for polymers with Young's modulus below 2 GPa, the volume fraction of ceramic required for the composite electrolyte to satisfy the mechanical stability criteria is above 50%. Therefore, traditional composite electrolytes with low loadings of inert fillers do not meet the mechanical property requirements.

In this regard, our strategy is to make a composite of a polymer electrolyte and a cation-conducting ceramic electrolyte wherein the ceramic loading is much higher than the traditional composite electrolytes. The stiffness of the ceramic electrolyte will prevent lithium dendrite growth, while the polymer electrolyte provides a high degree of resistance to volumetric strain and protects lithium anode. Due to the higher conductivity of the ceramic electrolyte, we aim to develop a mechanically strong composite electrolyte that has just enough polymer to conduct lithium from one conducting ceramic particle to another and thereby bridges the gap between the ceramic particles.

To develop such composites, we chose PEO + lithium trifluoromethanesulfonate (LiTf) as a model polymer electrolyte and lithium ion conducting glass ceramic (LICGC™) obtained from Ohara Corporation as a model ceramic electrolyte. LICGC™ has a NASICON structure with a base composition of  $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{P}_2\text{O}_5-\text{TiO}_2-\text{GeO}_2$

and high room temperature ionic conductivity ( $10^{-4} \text{ S cm}^{-1}$ ). LICGC™ is resistant to heat and is not sensitive to air,  $\text{CO}_2$  and water, as opposed to the case of  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ . The presence of titanium in the composition makes LICGC™ less stable with metallic lithium due to the reduction of  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$  [12]. In our earlier report, we studied the interfacial resistance between PEO based polymer electrolytes and sintered LICGC™ plate. A zero to positive interfacial resistance was identified by constructing laminated bilayer of PEO + lithium salt and LICGC™ plate using a dry fabrication protocol [13]. In this work, to achieve high volume fraction of ceramic in the composite electrolyte we adopted a highly versatile and scalable wet protocol using aqueous spray coating technique. The effects of processing methods, the addition of plasticizer and varying quantities of each component on the ionic conductivity of the composite electrolyte were thoroughly investigated. The physical, structural and thermal properties of the composites were exhaustively characterized by gas pycnometer, Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM), thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC).

## 2. Methods

### 2.1. Preparation of polymer and composite electrolytes

All the materials were dried for accurate weight measurements prior to preparation of solutions and slurries. PEO (Aldrich, average  $M_w = 600,000 \text{ g mol}^{-1}$ ) was dried at  $50^\circ\text{C}$  under vacuum for 16 h. Lithium trifluoromethane sulfonate (LiTf) (Aldrich, 97%) was dried at  $120^\circ\text{C}$  for 48 h in a vacuum oven inside a glove box. For work presented here, deionized water was used as a solvent. A dilute aqueous solution of 4 wt% PEO was prepared using a roller mill at low speed. A second solution of 5 wt% LiTf in water was prepared. Tetraethylene glycol dimethyl ether (TEGDME) (Aldrich, > 99%) was stored over molecular sieves to prevent moisture. The ceramic, LICGC™ powders, were obtained from Ohara Corporation. The LICGC™ particles have an average size of  $1 \mu\text{m}$ , with a particle size distribution of 0.4–1.4  $\mu\text{m}$ .

The polymer electrolyte solution was formed by blending PEO and LiTf solutions in a ratio that results in 16:1 atomic ratio of PEO ether oxygens per dissolved  $\text{Li}^+$  ion. The polymer electrolyte (PE) membranes were prepared by casting the solution onto a glass plate, followed by slow evaporation of the solvent over about 24 h. Drying was continued at room temperature in the antechamber of an argon glove box for 16 h, followed by further drying at  $80^\circ\text{C}$  in a vacuum oven inside the glovebox for 16 h. The dried polymer electrolyte membrane was gently peeled off from the glass plate for electrochemical, spectroscopic and density measurements. Polymer electrolyte samples containing TEGDME as a plasticizer were prepared and dried using the same method as PE without plasticizer, assuming there is little or no loss of TEGDME during drying. The molar ratio of TEGDME molecule per dissolved  $\text{Li}^+$  ion was 2:1.

To prepare a polymer-ceramic composite electrolyte (CPE), a 2.5 wt % suspension of LICGC™ ceramic in deionized water was prepared using probe sonication (Sonics & Materials, Inc, 50 Watts & 20 kHz). The LICGC™ suspension was mixed with calculated quantities of polymer electrolyte solution and further sonicated for 1 min. Spray coating was performed using an in-house setup with an airbrush (Paasche TG-3F) operating with compressed air at 30 psi. A thin layer of the composite electrolyte was sprayed on copper foil followed by drying with a heat gun. Spraying and drying process was repeated until the desired thickness ( $\sim 50\text{--}70 \mu\text{m}$ ) of the composite electrolyte was reached. The spray coated composite electrolyte was dried in the antechamber of an argon glove box at room temperature for 16 h, transferred into the glove box and further dried at  $80^\circ\text{C}$  in a vacuum oven for 16 h. All electrolyte samples are stored under argon atmosphere thereafter to minimize moisture exposure.

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