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Gel Composite Electrolyte - An Effective Way to Utilize Ceramic Fillers in Lithium Batteries

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Abstract

Achieving synergy between ion-conducting polymers and ceramics in a composite electrolyte has been proven to be difficult as the complicated ceramic/polymer interface presents challenges to understand and control. In this work, we report a strategy to utilize discrete ceramic fillers to form a gel composite electrolyte with enhanced transport properties for lithium metal batteries. The matrix of the composite membrane is crosslinked poly(ethylene oxide) with bis(trifluoromethane)sulfonimide lithium salt (LiTFSI). The membrane is plasticized with tetraethylene glycol dimethyl ether (TEGDME). The incorporation of doped-lithium aluminum titanium phosphate particles (LICGCTM) into the membrane greatly improves the membrane's cycling characteristics against the lithium electrode, exhibiting lower interfacial impedance, lower overpotential and higher rate capability. The underpinnings of the superior performance of the gel composite electrolyte is discussed in depth. LICGC[™] can immobilize the TFSI⁻ anions in the polymer matrix and simultaneously promote Li⁺ transport by increasing the plasticizer to Li⁺ ratio. Further, the transport enhancement is achieved without sacrificing mechanical properties. The composite membrane shows significantly improved handleability and processability. This work sheds light on the design strategy for a safe electrolyte towards stable Li metal batteries.

Introduction

Polymer electrolytes (PEs) with their intrinsic safety has demonstrated great potential to replace flammable liquid electrolytes in lithium-ion batteries.¹⁻³ The nonflammable nature and chemical stability allow them to be paired with the ultimate anode – lithium metal, which is the path to greatly improved energy and power densities.⁴ Poly(ethylene oxide) (PEO) based PEs are the most widely used polymer electrolyte material in lithium batteries.⁵ The ether oxygens in PEO can coordinate with Li⁺, which aids Li⁺ transport across the electrolyte membrane. However, Li⁺ transport commonly takes place in the amorphous phase of PEO, but linear PEO is semi-crystalline below ~66 °C. ^{6, 7} The presence of crystalline regions results in a low room-temperature ionic conductivity ($10^{-5} - 10^{-8}$ S/cm) for linear PEO based electrolytes. ^{8, 9} Li⁺ transport is also affected by the quantity and mobility of dissociated charge carriers. Another drawback of PEO-based PEs

is their low Li⁺ transference number, $t_{\text{Li}+} \sim 0.2$ to 0.6.¹⁰ In contrast, inorganic ceramic electrolytes have $t_{\text{Li}+}$ of 1.¹¹

A proposed strategy to enhance the ionic conductivity of PEs is to use a polymer-ceramic composite approach.¹²⁻¹⁸ This approach has been the focus of our group in recent years.¹⁹⁻²³ By incorporating highly conductive ceramic fillers into a polymer electrolyte host, the goal is to find a significant increase in the composite's conductivity. However, our past results indicate that without the use of plasticizers, only a mild increase in the ionic conductivity was achieved with the incorporation of low loadings of ceramic (< 10 vol%). This is consistent with many literature reports.^{12, 24} At medium to high loadings (> 30 vol%), the ionic conductivity of the composite electrolyte decreased dramatically compared to the neat polymer electrolyte.^{21, 22} Similar conclusions were reported by the Goodenough group using different materials to form composites.²⁵ Without the use of plasticizers, the lack of meaningful improvement of the ionic conductivity in polymer-ceramic composites arises from a large interfacial resistance between the polymer and the ceramic electrolytes.^{20, 26, 27} This prevents effective ion transport through the ceramic phase when particles are homogeneously dispersed in the polymer matrix. Further, the ceramic-Li salt interactions may lead to decreased ionic conductivity of the polymer phase.^{21, 22} In order for the conducting ceramic fillers to actively participate in ion conduction, the ceramic phase needs be made continuous and interconnected. Cui,28, 29 Hu,30, 31 our group23 and several other groups³²⁻³⁴ investigated in this so-called polymer-in-ceramic design and achieved success. However, one drawback of this design is that high temperature sintering is required to make a connected ceramic scaffold, which increases manufacturing cost.

In this work, we seek strategies to effectively utilize dispersed ceramic fillers in a polymerceramic composite electrolyte. Instead of using a dry polymer host as in previous work, we adopt a crosslinked PEO-based gel polymer electrolyte as the polymer matrix. In a gel polymer electrolyte (GPE), the crosslinked network serves as a host for the plasticizer and a controllable amount of plasticizer can be infused.³⁵⁻³⁹ Compared with traditional liquid electrolytes, GPEs incorporate plasticizers within the polymer matrix, thereby avoiding the leakage issue and reducing the flammability of organic plasticizers. A topic under intense investigation in the GPE field is the search for a suitable non-flammable plasticizer that also promotes high ionic conductivity. The plasticizer for the GPE in this work is tetraethylene glycol dimethyl ether (TEGDME).

A doped lithium aluminum titanium phosphate (LATP) ceramic, LICGCTM, is used as the model ceramic filler. We investigate the effects of incorporating LICGCTM on the physical, thermal, mechanical, ion transport and electrochemical properties of the gel composite electrolytes. The results show that the addition of LICGCTM into the gel polymer electrolyte resulted in much improved cycling characteristics against Li metal. The gel composite electrolyte exhibits lower interfacial impedance with Li, lower overpotential and higher rate capability. The improvement arises from two synergistic effects from LICGCTM: 1) LICGCTM can immobilize the anions in the polymer matrix, leading to a 2-fold increase in the Li⁺ transference number. 2) The presence of LICGCTM leads to increased plasticizer to Li⁺ ratio, which enhances Li⁺ dissociation and mobility. These synergistic effects lead to improved cycling performance of the gel composite electrolyte. Further, the transport property enhancement is achieved without sacrificing the mechanical properties of the membrane. Rather, the composite electrolyte exhibits significantly improved processability and handleability and can be made much thinner than the polymer electrolyte.

Experimental

Materials

O,O'-Bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-blockpolypropylene glycol (Jeffamine ED-900, Sigma-Aldrich) and poly(ethylene glycol) diglycidyl ether (PEGDGE, average M_n 500, Sigma-Aldrich) were used as received without further purification. Lithium bistrifluoromethanesulfonimide (LiTFSI) was purchased from 3M and dried in a vacuum furnace inside an Ar filled glovebox at 150 °C for 24 hours prior to use. Tetraethylene glycol dimethyl ether (TEGDME, Sigma-Aldrich) was dried on molecular sieves prior to use. Both LiTFSI and TEGDME were stored in an Ar filled glovebox after drying. Lithium-ion conducting glass ceramic powder (LICGCTM) was purchased from Ohara Corporation. It is a doped LATP ceramic with the general composition of Li₂O-Al₂O₃-SiO₂-P₂O₅-TiO₂-GeO₂. It is air and water stable. The average particle size of the powder used was 1 μ m.

Membrane fabrication

To prepare the polymer electrolyte membrane, Jeffamine and PEGDGE were mixed in a weight ratio of 9:10 at room temperature under constant stirring for 2 hours. LiTFSI was then added to the mixture and stirred for another 2 hours, until it was fully dissolved. The weight ratio of LiTFSI to Jeffamine+PEGDGE was 1:4. The liquid mixture was poured into an aluminum dish and cured at 100°C under vacuum for 16 hours. The crosslinked membrane was gently peeled off the aluminum dish and transferred into an argon glovebox and dried further inside the glovebox in a vacuum furnace at 80 °C for 16 hours.

Ceramic-containing composite electrolyte membranes were prepared by adding calculated weights of LICGCTM particles into the Jeffamine/PEGDGE/LiTFSI mixture. A small amount of ethanol was added into the mixture to aid the dispersion of LICGCTM. The mixture was then ball

milled for 10 minutes and cast on a Teflon substrate with a doctor blade. The Teflon substrate was preheated to 60 °C to allow the rapid evaporation of ethanol. The drying procedure of the composite electrolyte membranes was the same as that of the polymer electrolyte membrane.

After thorough drying of the polymer and composite electrolyte membranes, they were ready for use in the dry state. To prepare gel polymer and gel composite membranes, a piece of dry membrane was allowed to soak in TEGDME for 1 hour in an Ar glovebox.

Scanning Electron Microscopy (SEM)

SEM images were collected using a TM3030Plus Tabletop Microscope from Hitachi. The accelerating voltage used was 15 kV.

Differential Scanning Calorimetry (DSC)

DSC measurements were performed using a TA Instruments Q100 DSC. The samples were sealed in DSC sample pans in an argon filled glovebox. The samples contained at least 5 mg of polymeric material. DSC scans were run between -80 °C and 150 °C at a 5 °C/min scan rate under a nitrogen flow of 50 mL/min. The second cycle was used to calculate the glass transition temperature (T_g) of the sample.

Dynamic mechanical analysis (DMA)

DMA measurements were performed on the plasticized films using a TA Instruments RSA-G2 solid analyzer. A small tensile strain of 0.1 - 0.3 % was applied at 10 Hz. Measurements were taken between 20 °C and 90 °C under nitrogen flow. Samples were sealed inside the glovebox to minimize air exposure during the transfer to the instrument.

AC impedance measurements

Conductivity measurements were taken using a Biologic SP-300 from 7 MHz to 0.1 Hz with an AC voltage of 100 mV. Samples were equilibrated for 1.5 hrs at each temperature increment before the measurement was taken. Dry and plasticized polymer and composite electrolyte membranes were punched into ¹/₂ inch disks and sandwiched between two polished stainless steel rods. The sample was sealed with two layers of heat shrink tubing. The resultant Nyquist plots were fit using equivalent circuits and the bulk resistance of the polymer and composites was used to calculate the conductivity.

Electrochemical measurements

To perform Li symmetrical cell measurements, gel polymer and composite electrolyte membranes were sandwiched between two Li electrodes in CR2032 coin cells, which were assembled in an argon filled glovebox. Lithium electrodes were cleaned with a brush to remove the oxide layer, then rolled out using a clean and dry polypropylene bag to smooth the surface and cut into circles with a diameter of half inch. After soaking in TEGDME, the membranes were punched out to 5/8-inch diameter circles before assembling into the coin cell. The surface of the membranes was dabbed with Kimwipe to avoid flooding of TEGDME. The cells were cycled at room temperature on a Maccor tester. The AC impedance was measured before and after the cell cycling on a Bio-logic VSP. The frequency range of 1 MHz to 10 mHz and a voltage amplitude of 10 mV were applied for each measurement.

The full cells were assembled with $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622) cathode (BASF), gel polymer or composite electrolyte membrane and cycled with Li metal as the counter electrode. For full cell cycling, polymer and composite electrolyte membranes were plasticized with TEGDME. The NMC cathode was wet with 20 µL of LiPF₆ in EC/DMC as the catholyte. The cell components

were assembled into a standard CR2032 coin cell. Cycling was performed at room temperature on a Maccor equipment between 2.8 and 4.3 V versus Li+/Li.

Transference Number Measurements

Transference number measurements were taken using the Bruce and Vincent method with a Biologic SP-300.⁴⁰ Li symmetrical cells were cycled at 0.01 mA/cm² to form a stable interface between the electrolyte and Li. After cycling, the AC impedance spectrum was taken, and the cell was polarized for 10 hours at 10 mV, followed by another AC impedance measurement. The steady state transference number (t_{Li+}) was then calculated using Equation 1, where R_0 is the resistance measured prior to applying the potential (ΔV), I_0 is the initial current measured at the beginning of the polarization, and I_{SS} and R_{SS} are the steady state current and resistance measured after polarization.

$$\boldsymbol{t}_{Li+} = \frac{I_{ss}}{I_0} \left(\frac{\Delta V - I_0 R_0}{\Delta V - I_{ss} R_{ss}} \right) \ (1)$$

Results and Discussion

In this work we chose a crosslinked PEO-based membrane as the polymer matrix. The crosslinking precursors are Jeffamine and PEGDGE, which form a covalently linked network through the reaction between the amine on Jeffamine and the epoxide on PEGDGE (Fig. 1a). A previous report by Lehmann et al. shows that the precursors can crosslink with each other with moderate heat treatment without the use of any additives.⁴¹ After crosslinking and thorough drying, the polymer membrane readily absorbs liquid plasticizers and forms a gel. Linear PEO membranes, on the other hand, do not absorb liquid plasticizers easily at room temperature. Hence plasticizers are often mixed with linear PEO before membrane formation. This makes controlling the exact quantity of plasticizers in the membrane difficult because these plasticizers may be subject to evaporation or degradation during the membrane drying and annealing process.



Fig. 1 (a) Chemical structure of the components forming the composite electrolytes used in this work. (b) A photo of a composite electrolyte membrane with 50 wt% LICGCTM ceramic, ~60 μ m thick. The bending shows its flexibility. (c) A schematic of the gel composite electrolyte with Li⁺

conducting path. LICGCTM serves as an anion receptor and immobilizes TFSI⁻, and simultaneously TEGDME enhances Li⁺ dissociation and mobility. Schematic not drawn to scale.

The ceramic used in this work is an LATP type glass ceramic, LICGCTM, with the general composition of Li₂O-Al₂O₃-SiO₂-P₂O₅-TiO₂-GeO₂. It has high room temperature ionic conductivity (1 × 10⁻⁴ S/cm) and it is stable in air and water. The average particle size was 1 μ m. An SEM image of pristine LICGCTM particles is shown in Fig. 2a. These properties make LICGCTM the perfect candidate as the ceramic filler due to its compatibility with our film fabrication procedures. We note that all the ceramic loading values mentioned in the text refer to weight percent of the ceramic particles in the dry membranes.

We prepared composite electrolyte membranes using a simple one-pot procedure by mixing PEGDGE, Jeffamine, lithium salt (LiTFSI) and the ceramic particles, and the mixture was cast on a heated substrate using a doctor blade and cured at 100 °C. The detailed procedure is described in the Experimental section. After curing, a solid film formed on the substrate. The completion of the crosslinking reaction was confirmed by DSC and infrared (IR) spectroscopy (Fig. S1), where the absence of the crosslinking exotherm peak (DSC) and NH stretching vibration band (IR) was noted. Without ceramic fillers, the polymer electrolyte film could not be peeled from the substrate when the film thickness was below 100 µm as it was brittle and prone to tear.

The composite membranes with 50 wt% ceramic demonstrated significantly enhanced the handleability and could easily be made thinner than 100 µm. Fig. 1b shows a picture of the composite electrolyte with 50 wt% ceramic, easy to bend and manipulate with a thickness of ~60 µm. With 70 wt% ceramic loading, the film became brittle again. At this loading the estimated volume fraction of the ceramic is 51 vol%. SEM images of dry composite electrolyte membranes with 30, 50 and 70 wt% ceramic are shown in Fig. 2b-d. The LICGC[™] particles dispersed homogeneously in composites with 30 and 50 wt% ceramic. At 70 wt% loading, pinholes are observed in the membranes. We make a note here that even above the percolation threshold loading, the ceramic particles will not have good particle-particle contact due to their high modulus and low effective contact area. In another related work, we partially sintered the LICGC[™] ceramic and created a three-dimensionally connected network.²³ The morphological differences between densely packed but unconnected discrete ceramic particles and an interconnected

ceramic network with good necking between particles is shown by the SEM images in

Fig. S2.

After curing and thorough drying of the composite membranes, they were plasticized

with TEGDME. A schematic of the components of plasticized composite membranes is

shown in Fig. 1c. The matrix of the membrane is a crosslinked network of PEO, with salt



(LiTFSI), plasticizer (TEGDME) and ceramic particles (LICGC[™]) dispersed in it.

Fig. 2 SEM images of (a) pristine LICGCTM ceramic particles and (b-d) dry composite electrolyte membranes with (b) 30 wt %, (c) 50 wt %, and (d) 70 wt % LICGCTM ceramic. The scale bar in (a) represents 10 μm and it applies to all the images.



Fig. 3 (a) DSC thermograms of dry polymer and composite electrolyte membranes. Plots are vertically shifted for clarity. (b) storage moduli of polymer and composite electrolyte membranes plasticized with TEGDME.

Table 1 Glass transition temperature (T_g) and TEGDME content of polymer and

composite electrolyte membranes.

Ceramic loading (wt%)	7 _g (°C)*	TEGDME uptake (%)	TEGDME volume fraction (%)	Dimensional swelling (%)	TEGDME/Polymer (w/w)	TEGDME/LiTFSI (w/w)
0	-36.0	72.5	50.1	56.8	0.91	3.6
30.0	-39.1	78.6	56.6	72.0	1.32	5.6
50.0	-40.5	52.7	50.0	30.1	1.40	5.3
70.0	-40.6	46.2	50.8	_**	1.92	7.7

*The T_g values are from the dry membranes.

**Film was too fragile to measure.

We evaluated the thermal and mechanical properties of the polymer and composite electrolyte membranes using DSC and DMA (Fig. 3). The DSC thermograms of dry polymer and composites are shown in Fig. 3a. The crystallinity of PEO is largely suppressed by crosslinking, with the exception of the 50 wt% sample, where a small endothermal peak is still observed at 63.2 °C. The glass transition temperature (T_g) of these samples is tabulated in Table 1. The addition of ceramic into the polymer electrolyte membrane decreased the T_g of PEO segments. This decrease is consistent with our previous results using a linear PEO-based polymer electrolyte as the matrix. The ceramic particles can act as "solid plasticizers" and decrease the T_g of the polymer matrix.^{42, 43} The decrease in T_g is associated with increased segmental mobility which favors ion transport. The T_g of the TEGDME-

plasticized samples could not be measured as the TEGDME crystallization occurs at around -45 °C which masked the region in which the T_{α} would be observed.

TEGDME was introduced into the polymer and composite electrolyte membranes by immersing thoroughly dried membranes in TEGDME in a sealed container inside an Ar filled glovebox. The membranes started swelling immediately upon immersion. TEGDME uptake, defined by Equation 2, was obtained at 10 min, 30 min, 1 h, 4 h and 16 h of soaking to gauge the uptake kinetics (Fig. S3). The thinner composite membranes with less than 100 µm thickness reached saturated uptake within 10 min. The thicker pristine polymer membrane reached saturated uptake in 1 hour. After 1h, TEGDME uptake stayed constant, indicating that a saturated amount of plasticizer had been absorbed. Based on this data, all the membranes were allowed to soak in TEGDME for 1 h prior to other measurements. It is worth mentioning that we did not observe salt leaching out of the membranes within the soaking times investigated.

$$TEGDME uptake = \frac{Weight of wet membrane - Weight of dry membrane}{Weight of dry membrane} \times 100\%$$
(2)

The effect of ceramic particles on the TEGDME content of the films is shown in Table 1. TEGDME uptake first increased at 30 wt% ceramic loading and then decreased above 50 wt% loading. The dimensional swelling of the films, defined by Equation 3, was calculated by measuring the dimensions of the films before and after TEGDME soaking. The film with 30 wt% ceramic exhibited more swelling (72.0%) compared to the pristine polymer film (56.8%). The film with 50 wt% ceramic exhibited significantly less swelling (30.1%) compared to the pristine polymer film.

Dimensional swelling = $\frac{\text{Volume of wet membrane} - \text{Volume of dry membrane}}{\text{Volume of dry membrane}} \times 100\%$ (3)

The trend of the TEGDME uptake and dimensional swelling as a function of ceramic loading may be unclear at first sight. But if we calculate the weight ratio of TEGDME to the polymer in each film, it becomes clear that as ceramic loading increases, TEGDME/polymer ratio increased. Since the weight ratio of LiTFSI to polymer was fixed at 0.25, TEGDME/Li⁺ ratio also increased with increasing ceramic loading. At the same time, with increasing ceramic loading, the polymer's volume fraction decreased, so the volume fraction of TEGDME with regard to the total volume of the membrane stayed approximately the same, ~ 50 vol%.

The storage and loss moduli of plasticized membranes were measured by DMA (Fig.

3b). The loss moduli were too low to be captured by the equipment and hence are not shown. Membranes with 30 and 50 wt% ceramic particles showed similar storage moduli to the polymer electrolyte membrane without ceramic, between 2 and 3 MPa. The composite membrane with 70 wt% ceramic showed a two-fold increase in storage modulus, approximately 4.5 MPa.

The above results revealed that with increasing ceramic content, the ratio of TEGDME/polymer and TEGDME/Li⁺ increased. On the other hand, the absolute TEGDME content of the films did not change significantly. As a result, the mechanical modulus of the plasticized films remained the same for the composite films with 30 wt% and 50 wt% ceramic. We note that commonly there is a tradeoff between the plasticizer content and mechanical properties of the films. In our work, with the addition of ceramic fillers, we were able to increase the plasticizer to Li⁺ ratio without sacrificing the mechanical properties of the membranes. Further, the film with 50 wt% ceramic exhibited improved resistance to dimensional swelling. This film also showed significantly improved

handleability and processibility, and could easily be made thinner than 100 µm. The

benefit of increased plasticizer to Li⁺ ratio will be discussed later in the manuscript.



Fig. 4 Ionic conductivity of polymer and composite electrolytes as a function of inverse

temperature, (a) in the dry state, (b) plasticized with TEGDME. (c) Li⁺ conductivity of

plasticized polymer and composite electrolytes.

Table 2 Ionic conductivity, σ , at 30 °C, activation energy E_a and Li⁺ conductivity of

Ceramic Ioading (wt%)	σ (dry) at 30 °C (S/cm)	<i>E_a</i> (dry) (eV)	σ (TEGDME) at 30 °C (S/cm)	<i>E</i> _a (TEGDME) (eV)
0	8.2 × 10 ⁻⁶	0.55	1.3 × 10 ⁻⁴	0.23
30	3.9 × 10⁻ ⁶	0.51	1.5 × 10⁻⁴	0.25
50	7.9 × 10 ⁻⁶	0.45	1.2 × 10 ⁻⁴	0.23
70	1.3 × 10 ⁻⁶	0.55	2.2 × 10⁻⁵	0.23

polymer and composite electrolyte membranes.

The ionic conductivity, σ , of the polymer and composite membranes in dry and plasticized states are shown in Fig. 4. The error range was calculated based on repeats of 3 samples. Representative Nyquist plots to extrapolate σ values are shown in Fig. S4. The conductivity at 30 °C as well as the activation energy, E_a , are tabulated in Table 2. Dry polymer electrolyte without ceramic particles has a σ of 8.2 × 10⁻⁶ at 30 °C, which is relatively low. In the dry state, although the crystallinity of PEO segments are suppressed, the crosslinked network acts as "anchors" which slow down the dynamics of PEO chains. The slow dynamics leads to low conductivity.

Dense LICGCTM plate's conductivity is displayed in Fig.4 together with the composite membranes. Dense LICGCTM's conductivity is one to two orders of magnitude higher than the dry polymer electrolyte. However, the incorporation of ceramic particles into the dry membranes led to decreased ionic conductivity (Fig. 4a). The underpinnings for the decreased ionic conductivity in dry composite electrolytes are two-fold: 1. It is discovered that there is a large interfacial resistance for ion transport between PEO based electrolytes and LICGC[™] ceramic.²⁰ When discrete ceramic particles are mixed with a dry polymer electrolyte, the large interfacial resistance prevents the ceramic particles from effectively contributing to ion conduction. 2. Due to interactions between the surface of LICGC[™] ceramic and the Li salt in the polymer, the mobilities of Li⁺ cation and the anion as well as the segmental mobility of the PEO chains are found to decrease. This leads to decreased conductivity of the polymer phase with the addition of LICGC[™] ceramic^{22, 44}.

The change in σ as a function of ceramic loading in the dry membranes was not monotonic – σ of composite electrolyte with 50 wt% ceramic was higher than that with 30 wt% ceramic. There may be multiple factors at play: the incorporation of the ceramic decreased the T_{q} of the PEO segments, which leads to increased σ . At the same time, as the ceramic loading increases, there is more resistive interfacial area, which decreases σ . The opposite effects compete with each other and resulted in the non-monotonic trend. σ of the composite membrane with 70 wt% ceramic is an order of magnitude lower compared to the dry polymer. At this loading, the polymer phase's volume fraction was estimated to be 49%. The polymer phase may exhibit greatly increased tortuosity and may have lost continuous ion conduction pathways, as pinholes were observed in this membrane (Fig.2c).

When plasticized with TEGDME, σ of both the polymer electrolyte and the composite electrolytes increased by 1-2 orders of magnitude (Fig. 4b), and E_a decreased to approximately half (from ~0.5 eV down to ~0.23 eV) (Table 2). A combination of mechanisms, including an increase of Li⁺ dissociation in the polymer, increased

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segmental dynamics, and change of ion transport mechanism from hopping to vehicular transport may be the origin of this increase. σ of composite electrolytes with 30 and 50 wt% ceramic is similar to the polymer electrolyte without any ceramic, within experimental error. Compared to the dry membranes, the negative impacts of the ceramic filler on the ionic conductivity is eliminated by the presence of the plasticizer. The composite membrane's conductivity plasticized with a different solvent, dimethyl carbonate (DMC), was evaluated and similar conductivity was obtained (see Electronic Supplementary Information Fig. S5). At 70 wt% ceramic loading, σ was low even with the presence of plasticizers. This is likely due to the increased tortuosity or loss of connectivity of the polymer phase. Li⁺ conductivity in these membranes was calculated based on the transference number measurements (Fig. 4c) and will be discussed in detail later in the manuscript.

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Fig. 5 Li symmetrical cell cycling with polymer and composite electrolyte membranes plasticized with TEGDME. (a) 100 hours of cycling at 50 μ A/cm² at room temperature. (b) corresponding detailed cycling from 40 to 42 hours, and (c) impedance spectra of the membranes before and after 100 hours of cycling at 50 μ A/cm². Inset of (c), high frequency part of the impedance spectrum of the gel polymer electrolyte before cycling.

(d), 100 hours of cycling at 100 μ A/cm² at room temperature.

Li symmetrical cell cycling was performed on the TEGDME plasticized gel polymer and gel composite electrolyte with 50 wt% ceramic, shown in Fig. 5. For convenience of comparison we refer to these two electrolytes as GPE and GCE-50. The cells were cycled at 50 µA/cm² at room temperature. Detailed cycling procedure is described in the Experimental section. The cell containing GCE-50 showed much lower overpotential, 0.04 V versus the cell containing GPE, 0.13V (Fig. 5a). Fig. 5b shows detailed time dependence of the cycling profiles of these two cells from 40 to 42 hours. For the GPE cell, the voltage profile never reached a steady-state plateau in the given cycle time (15 min). The end potential was approximately 0.13V. In contrast, the cell with GCE-50 electrolyte quickly reached a steady-state plateau potential of 0.036 V.

The impedance of the Li symmetrical cell with GPE and GCE-50 was taken prior and after 100 hours of cycling (Fig. 5c). Both cells showed a prominent semicircle and a short tale inclined at 45 degrees. A closer look of the semicircle (inset of Fig. 5c) revealed that it is a convolution of a very small semicircle at high frequency and a large semicircle at medium frequency. The small high frequency semicircle is related to the bulk resistance of the electrolyte films. This is consistent with the Nyquist plot of the electrolytes with blocking electrodes (Fig. S4). The diameter of the large semicircle represents the electrolyte's interfacial impedance with Li electrodes, which includes two interfacial processes – ionic conduction through the passive layer and electrode charge transfer.⁴⁵ The short tale is associated with the diffusion process into the electrolyte.⁴⁵ GCE-50 had a much smaller initial interfacial impedance ($360 \ \Omega \cdot cm^2$) with Li electrodes compared to the GPE ($750 \ \Omega \cdot cm^2$). After 100 hours, the interfacial impedance increase was much smaller for GCE-50 ($560 \ \Omega \cdot cm^2$), compared to the GPE ($1500 \ \Omega \cdot cm^2$). The increase in the interfacial impedance is associated with the growth of the passive layer formed at the electrolyte-Li interface. This result suggests that the passive layer grows slower in GCE-50, indicating better stability with Li.

Further, GCE-50 exhibited higher rate capability (Fig. 5d). At the current density of $100 \ \mu$ A/cm², GPE showed unstable cycling profile and died after 95 hours. GCE-50, on the other hand, exhibited stable cycling. Overall, these results show that the addition of ceramic particles to the gel polymer electrolytes led to lower interfacial impedance with Li metal, increased stability, lower overpotential and higher rate capability.



Fig. 6 (a) Charge and discharge curves of full cell NMC622|GPE|Li at cycle number 1, 2, 3, 6 and 7 and (b) cycling performance of the cell in (a). (c) Charge and discharge curves of full cell NMC622|GCE-50|Li at cycle number 1, 5, 10, 15, 20 and 30 and (d) cycling performance of the cell (c).

We evaluated GPE and GCE-50's cycling performance in full batteries, shown in Fig. 6. The full cells were assembled using NMC622 cathode, TEGDME plasticized membranes and Li metal anode. The cells were cycled at current densities of 0.05, 0.1, 0.2 and 0.3 mA/cm² between 2.8

and 4.3 V, at room temperature. In a recent publication by Homann et al.⁴⁶ it is demonstrated that PEO based polymer electrolyte can potentially sustain high voltage cathode such as NMC622, as the oxidation onset is above the working potential of NMC622. The authors argue that the polymer | NMC622 interface is unlikely to be the primary source of cell failure indicated by the "voltage noise". Instead, the Li | polymer interface is the main source. Based on the results of this work, we evaluated our PEO-based electrolytes with an NMC cathode. In order to cycle the cells, the NMC cathode was wet with 20 µL of LiPF₆ in EC/DMC as the catholyte. At the lowest current density tested, 0.05 mA/cm², both the GPE and GCE-50 cells cycled well. The initial discharge capacity was relatively low, probably because good wetting of the catholyte with the cathode particles was still forming. After the first cycle, stable discharge capacity and good Coulombic efficiency (>99.5%) were achieved for both cells. At higher current densities (≥ 0.1 mA/cm²), the GPE cell could not cycle. In contrast, GCE-50 showed good cycling performance at 0.1 and 0.2 mA/cm². The discharge capacity started showing significant decrease at 0.3 mA/cm². The full cell cycling results are consistent with the Li symmetric cell cycling performance, further proving that adding LICGC[™] ceramic significantly improves the cycling performance of the gel electrolytes.

We also tested the cycling performance of membranes with 30 and 70 wt% ceramic (data not shown). 50 wt% turns out to be the optimum loading that gives the best performance. The

membrane with 30 wt% ceramic behaved similar to pristine polymer membrane and the one with 70 wt% ceramic did not have good transport properties due to defects. In the dry membrane, 50 wt% ceramic corresponds to an estimated volume fraction of 31.4 vol%. After soaking in TEGDME, the ceramic volume fraction in GCE-50 decreased to 15.7 vol%, due to the absorption of TEGDME. Therefore the optimum ceramic loading in the gel composite electrolyte is relatively low. To further improve the performance, efforts need to be focused on increasing the interfacial area between the ceramic and the polymer – e.g. decreasing the particle size from micron level to nanometer level.

It is worth mentioning that the goal of this work is to develop design rules to best utilize discrete ceramic particles in a composite electrolyte. The Li symmetric cell and full cell performance shown in this work is to demonstrate the benefit of ceramic fillers in a plasticized gel membrane. Further optimization, such as cathode design and ceramic filler composition, is needed to produce ultimate cycling performance.

We now take an in-depth examination of the underpinnings for the improved cycling performance from the gel composite electrolyte GCE-50. The shape of the Li symmetrical cell cycling curve can give a lot of information about the electrolyte (Fig.5b). In a recent report, Pesko et al. used a transient model to predict the time-dependence of potential in a symmetric cell during cycling.⁴⁷ In each plating/stripping cycle, the potential increases

with time due to the formation of concentration gradients in the electrolyte. The potential profile will plateau when the cell reaches steady-state. The fact that GPE never reached the steady-state plateau suggests that a relatively large concentration gradient is forming in this electrolyte. In the given time of 15 min, the cell could not reach steady-state. In contrast, GCE-50 quickly reached steady-state, indicating that the concentration gradient is much smaller. Concentration gradient is known to cause cation depletion at the electrodes at high current densities. A smaller concentration gradient means that GCE-50 can sustain higher critical current density and has higher rate capabilities.

We then measured the electrolytes' Li⁺ transference number, t_{Li+} , shown in Table 3. The steady-state t_{Li+} was measured using the Bruce-Vincent method⁴⁰. Details of t_{Li+} measurements are shown in Fig. S6. Compared to GPE ($t_{Li+} = 0.20$), t_{Li+} increased more than two times for GCE-50 ($t_{Li+} = 0.44$), confirming that GCE-50 indeed has a smaller concentration gradient at steady-state.

Table 3 Li⁺ transference numbers, t_{Li^+} , of plasticized membranes.



0	0.20	
50	0.44	

* t_{Li^+} was measured with plasticized membranes at room temperature



Fig. 7 Raman spectroscopy of the TFSI⁻ breathing stretch of dry electrolyte films. (a)

pristine polymer electrolyte, and (b) composite electrolyte with 50 wt% LICGC[™].

We used Raman spectroscopy to investigate the effect of LICGCTM particles on ion association in the polymer electrolyte, shown in Fig. 7. The CF₃ peak around 740 cm⁻¹, referred

to as the "TFSI breathing stretch" can be used as an indicator for dissociated/coordinated TFSI^{-,48} In the pristine polymer electrolyte membrane, a single Gaussian peak was observed at 741.8 cm⁻¹ (Fig. 7a), suggesting that the TFSI[−] anion is in a completely dissociated state. In the composite electrolyte containing 50 wt% LICGCTM, the TFSI[−] breathing stretch is a convolution of two peaks, one at 741.5 cm⁻¹ and another peak at 746.5 cm⁻¹ (Fig. 7b). The latter peak with increased Raman shift suggests that a portion of the TFSI[−] anions were bound. Peak fitting of the Raman spectra showed that 73% of the TFSI[−] anions were in the bound state. These Raman results revealed that the surface of LICGCTM is acting as an anion receptor and can immobilize TFSI[−] anions. This is the root cause of increased *t*_{Li+} observed in the composite electrolyte membranes.

The fact that LICGCTM particles can cause increased t_{Li+} in composite electrolytes has been observed in our past work with other PEO-based dry membranes.^{19, 49} However, in the dry membranes, the increase in t_{Li+} is offset by a significant decrease in the overall conductivity of the composite electrolyte. It is discovered that in the dry membranes, a decrease in the anion's mobility is accompanied by concurrent decrease in the cation's mobility, due to the association between the cation and the anion.^{21, 22} In the plasticized membranes, on the other hand, not only did the t_{Li^+} increase with the addition of LICGCTM, the overall ionic conductivity of GCE-50 remained similar to GPE (Fig. 4b). We calculated Li⁺ conductivity, σ_{Li^+} , of GPE and GCE-50 by using the simple equation below:

$$\sigma_{\mathrm{Li}\,+} = \sigma \cdot t_{\mathrm{Li}\,+} \qquad (4)$$

where σ is the overall conductivity of the membrane. The results are shown in Fig. 4c. Compared to GPE, there is a two-fold increase in σ_{Li*} for GCE-50. Although the volume fractions of TEGDME with regard to the total volume of GPE and GCE-50 are nearly identical, the addition of the ceramic caused increased TEGDME to Li* ratio, as discussed in previous paragraphs (Table 2, last column). The increase in TEGDME/Li* ratio provides more coordination sites for Li* and can lead to enhanced Li* dissociation and more Li* transporting via the vehicular mechanism. Both effects contribute to increased σ_{Li*} for GCE-50.

To this end, the efficacy of LICGCTM ceramic in plasticized membranes is clear: in GCE-50, LICGCTM serves as an anion receptor and immobilizes TFSI⁻, leading to significantly

increased t_{Li+} ; simultaneously, it promotes Li⁺ dissociation and enhances Li⁺ mobility due to increased plasticizer to Li⁺ ratio. The simultaneous Li⁺ transport promotion and TFSI⁻ immobilization leads to greatly improved Li-Li symmetrical cell cycling performance. A schematic of this mechanism is shown in Fig. 1c. Recall that GCE-50 has similar modulus to GPE (Fig. 3b) and much improved handleability and processability. Therefore in GCE-50, the transport property improvement is achieved without sacrificing mechanical properties.

Conclusions

In this work, we fabricated a gel composite electrolyte by incorporating an LATP-type ceramic, LICGCTM, into crosslinked PEO-based gel electrolyte membrane plasticized with TEGDME. The composite electrolyte with 50 wt% ceramic exhibited superior cycling performance against Li metal, showing lower interfacial impedance, lower overpotential and higher rate capability.

A close examination of the cycling profile revealed a much smaller concentration gradient in the composite electrolyte compared to the polymer electrolyte. This is confirmed by the transference number measurement – a 2-fold increase in the Li⁺ transference number in the composite membrane was obtained. Further, the presence of LICGCTM led to increased TEGDME to Li⁺ ratio due to decreased volume fraction of the polymer phase. This in turn enhanced Li⁺ dissociation and mobility in the composite membrane and caused a 2-fold increase in the Li⁺ conductivity. The cation transport promotion and anion immobilization together contribute to the superior performance of the gel composite electrolyte. Last but not least, the transport enhancement was achieved without sacrificing the mechanical properties of the membrane, as the volume fraction of TEGDME in the composite and polymer electrolytes was relatively constant. Rather, the composite electrolyte showed significantly improved handleability. This work on plasticized gel composite electrolytes, together with our past work on dry composite electrolytes, points to an important design strategy for composite electrolytes towards a stable Li metal anode: anion immobilization alone may not sufficiently improve the transport properties of the electrolyte; in order to improve the cycling performance against Li metal, we must consider synergistic anion immobilization and cation dissociation. If one additive (e.g. ceramic fillers) cannot achieve both effects, then adding another component (e.g. a plasticizer) may be necessary.

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