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Communication—Deconvoluting the Conductivity Enhancement due to Nanoparticle Fillers in PVdF-Based Polymer Electrolytes for Li-Metal Batteries

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Solid polymer electrolytes (SPE) possess significant advantages over inorganic solid electrolytes in terms of performance and flexibility, but suffer from low conductivities. To improve their conductivities, ceramic nanoparticle fillers are typically used as additives. However, the conductivity enhancement could arise from both Li^+ ions and surface-adsorbed moisture/protonic groups on the nanoparticles. Here, to deconvolute these effects, we report the synthesis and performances of polyvinylidene fluoride (PVdF)-based SPEs using a model filler, TiO_2, in as-received and annealed conditions. We find that there could be moderate contribution from non-Li^+ species, and emphasize the need to anneal the additives prior to their incorporation.

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Lithium-ion batteries have revolutionized the development of portable energy storage devices for over three decades.[1] Ongoing efforts in the community focus on increasing the energy density of the state-of-the-art Li batteries to greater than 450 Wh kg^{-1}, in order to make the driving range of electric vehicles equivalent to those with internal combustion engines.[2] One common strategy to increase the energy density of Li-ion batteries is to use Li metal as the anode because of its light weight and high volumetric capacity (2061 mAh cm^{-3}). However, the use of Li metal brings forth a host of other issues that need to be addressed. Most importantly, the high reactivity of organic electrolytes with Li metal leads to an uncontrollable growth of dendrites, which tend to disconnect from the bulk upon repeated cycling, resulting in the formation of "dead" lithium. In worse cases, dendrites could lead to short circuit, potentially posing a fire hazard.[3]

Solid electrolytes, with their high mechanical strength, possess an inherent ability to suppress the growth of dendrites,[4] thereby enabling the safe use of Li metal as the anode. While solid inorganic (ceramic/garnet) electrolytes possess high ionic conductivities, their cyclability with Li-metal is not good enough to project them in practical applications. On the other hand, polymer electrolytes, despite possessing average conductivities, offer better cyclability because of an intimate contact with the electrodes. Owing to this advantage, polymer electrolytes have already been commercialized in consumer applications. The most popular choice for the polymer host has been poly(ethylene) oxide (PEO), which however suffers from issues such as low ionic conductivity and poor mechanical properties.[5,6] The poor mechanical properties arise from the fact that PEO remains as a highly deformable, sticky membrane even after drying. Therefore, there is a considerable advantage in choosing rigid polymer hosts for electrolyte applications.

Polyvinylidene fluoride (PVdF), is a popular alternative that has been adopted in Li polymer batteries. However, it has almost always been used in combination with a Li-ion solvating solvent such as ethylene carbonate (EC), propylene carbonate (PC), and tetraglyme. This combination, known as "gel-polymer electrolyte," shows some improvement in safety aspects. However, it does not eliminate the safety concerns arising from the flammability of the solvent used. Moreover, to improve the specific energies and to enhance the safety of polymer-based batteries, it is important to eliminate the use of solvents and develop *solid* polymer electrolytes instead.

To improve the conductivities of solid polymer electrolytes up to the level of liquid electrolytes, additives such as ceramics and metal-oxide-based nanoparticles have been typically used.[7] However, the conductivity enhancement arising from such ceramics is often mistakenly, solely attributed to Li^+ ions. Since the typical conductivity tests using a blocking electrode setup cannot distinguish between the type of ions, the question of whether the surface-adsorbed moisture groups/protons of the metal-oxide nanoparticles could also contribute to the electrolyte's conductivity is rather unsettled. In order to deconvolute the effects of conductivity enhancement that occurs solely through Li^+ ions and that arises from surface-adsorbed protons, we report the synthesis and electrochemical performances of PVdF-based composite electrolytes with a model nanoparticle filler, TiO_2 in two different conditions: (i) as-received, and (ii) annealed. The plating/stripping behavior of these electrolytes are investigated and confirmed through the galvanostatic cycling of Li–Li symmetric cells.

Experimental

0.18 gm of lithium perchlorate ($LiClO_4$, Sigma-Aldrich, Inc.) was dissolved in 3 ml acetone. In a separate vial, 50 wt.% poly (vinylidene fluoride-*co*-hexafluoropropylene) (PVdF-HFP) pellets (Sigma-Aldrich, Inc.) were dissolved in a few ml of acetone at 40 °C and added to the $LiClO_4$ solution. This mixture was stirred in a magnetic stirrer at 40 °C for 12 h to get a clear, viscous polymer blend. Prior to the synthesis, $LiClO_4$, and PVdF-HFP were dried in vacuum for 12 h. For the preparation of nanocomposite polymer electrolytes, either 2 wt.% annealed TiO_2 or as-received TiO_2 nanoparticle powder (US Research Nanomaterials, Inc.) was added to this polymer blend and stirred further for 12 more hours. The annealed-TiO_2 sample was obtained by heating the TiO_2 nanoparticles at 100 °C in vacuum for 24 h. The polymer blend was spread onto a glass petri dish and left on a hotplate at 80 °C for 3 h to allow the solvent to evaporate. The resultant film was cut into disks of 15 mm diameter each and was used as electrolyte membranes in Li–Li symmetric cells.

Fresh Li chips (MTI Corp.) were used as electrodes in the symmetric cell tests. Their surfaces were scraped with a surgical blade until their shiny, metallic surfaces were revealed. Two such Li discs were placed on either sides of the polymer membrane, and this assembly was sealed in a coin-cell (CR 2032) set-up to obtain a Li | Li symmetric cell. Galvanostatic charge/discharge cycling, electrochemical impedance spectroscopy (EIS), DC polarization, and cyclic voltammetry (CV) experiments were performed using a Bio-Logic VMP3 multi-channel potentiostat/galvanostat equipped with EC-Lab software. The polymer electrolyte was sandwiched between two stainless-steel discs which act as blocking electrodes. The AC

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impedance spectra were measured in the frequency range of 200 kHz to 50 mHz. DC polarization on the Li | Li symmetric cell was carried out at a constant step voltage of 0.01 V. CV experiments were performed using a Li | Li symmetric cell at a sweep rate of 5 mV s^{-1}. Galvanostatic cycling of Li | Li symmetric cells were carried out at areal current densities of 0.05 mA cm^{-2} for a plating/stripping time of 0.25 h.

Results and Discussion

Although initial work on gel polymer electrolytes focused on pure poly(vinylidene fluoride) (PVdF), its copolymer, poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) has also received attention because of its lower crystallinity.[7–9] Moreover, pure PVdF, with a single monomer throughout the entire polymer chain, provides only less free volume to the mobile Li^+ ions.[7] Figures 1a–1b show the structures of monomers of poly(vinylidene fluoride) (PVdF), and poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP), respectively.

In contrast to PEO, the solid polymer electrolytes prepared with PVdF-HFP are known to have better mechanical integrity and conductivity.[10,11] Figure 1c shows the digital images of the solid polymer electrolyte, PVdF-HFP/$LiClO_4$ after drying. Figure 1d shows the membrane folded using a tweezer, thereby demonstrating its resilience. In general, when an inorganic non-conductive ceramic filler (such as Al_2O_3, SiO_2, and TiO_2) is added to polymer electrolytes, there is a noticeable improvement in their conductivities.[12–17] However, it has been speculated that Li^+ conductivity enhancement due to ceramic nanoparticles could only be minimal, and that there could be a contribution from the protons or other species adsorbed on to the surface of these metal oxide particles.[18,19] Therefore, to deconvolute the conductivity enhancement due to Li^+ ions and protons, two different polymer electrolyte samples were prepared: (i) PVdF-HFP/$LiClO_4$ with 2% as-received TiO_2, and (ii) PVdF-HFP/$LiClO_4$ with 2% annealed TiO_2. The latter sample was prepared with the intention of getting rid of any surface adsorbed moisture and protonic groups.

Cyclic voltammetry was used to investigate the plating/stripping behavior of these two solid polymer electrolyte samples. Figures 2a–2c show the first two cycles of the cyclic voltammograms of the PVdF-HFP/$LiClO_4$ sample, PVdF-HFP/$LiClO_4$/2 wt.% as-received TiO_2, and PVdF-HFP/$LiClO_4$/2 wt.% annealed TiO_2 samples, respectively. The occurrence of clear anodic and cathodic peaks in all cases serve as an evidence for Li plating/stripping in these dry SPE membranes. However, the intensity of anodic peak in PVdF-HFP/$LiClO_4$ sample (Fig. 2a) falls from the second cycle onwards, perhaps due to its low ionic conductivity. The CV plot in Fig. 2c also serves as an evidence of Li plating/stripping from the SPE with the inorganic ceramic fillers even upon annealing.

Typically, the area under the curve of a cyclic voltammogram is indicative of the amount of charge transferred during the electrochemical reaction.[20,21] In fact, it is even advantageous and more accurate to measure the charge rather than the current.[22] For this reason, a comparison of the areas under the curve of cyclic voltammograms will shed light on whether there were any differences in the amount of charge carriers in the systems. In Fig. S1 (available online at stacks.iop.org/JES/168/020525/mmedia) (Supporting Information), we compare the areas under the curves of the first cycles of cyclic voltammograms of PVdF-HFP/$LiClO_4$/as-received-TiO_2, and PVdF-HFP/$LiClO_4$/annealed-TiO_2. The charge in the

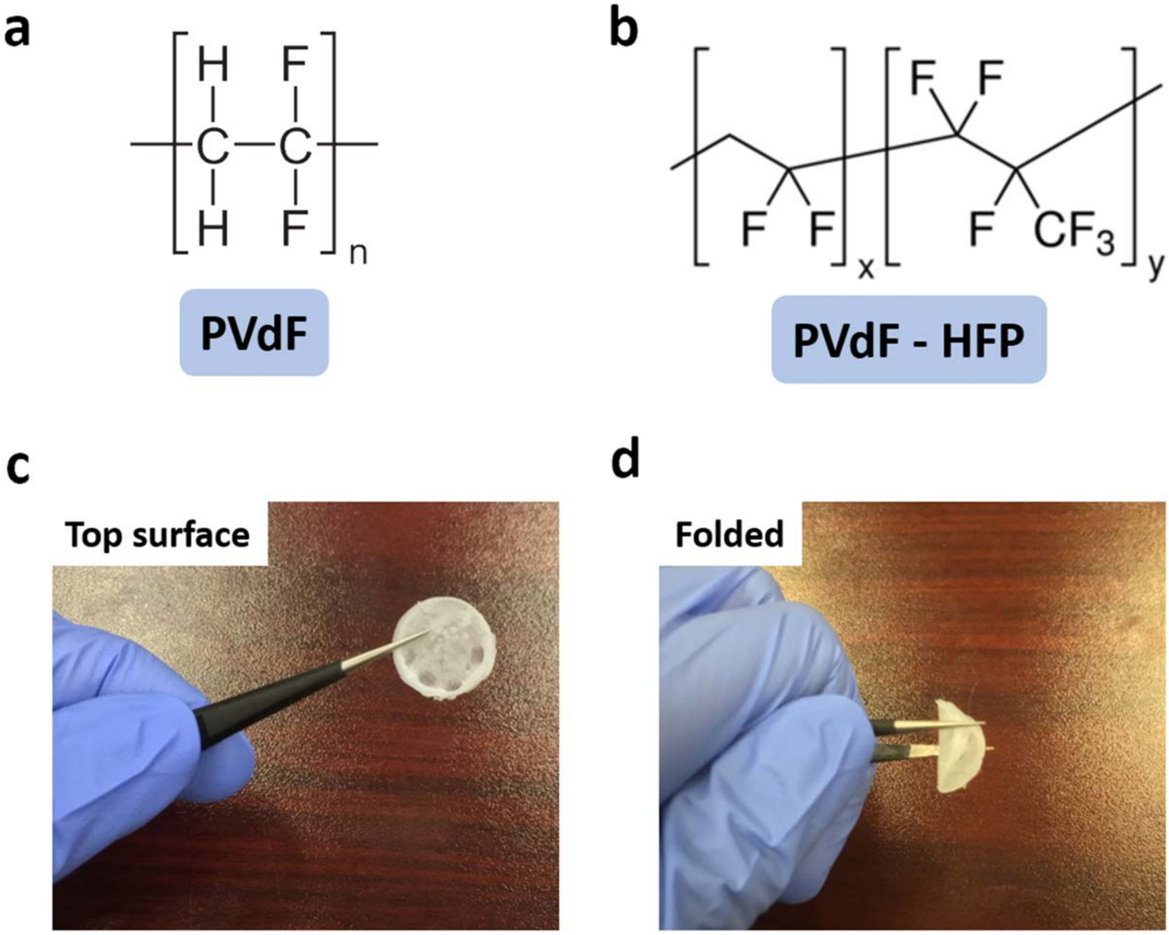

Figure 1. (a)–(b) Structure of the monomers of poly(vinylidene fluoride) (PVdF) (a), and poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) (b). (c)–(d) Digital photographs of the PVdF-HFP/$LiClO_4$ solid polymer electrolyte showing the top surface (c), and when the membrane is folded (d).

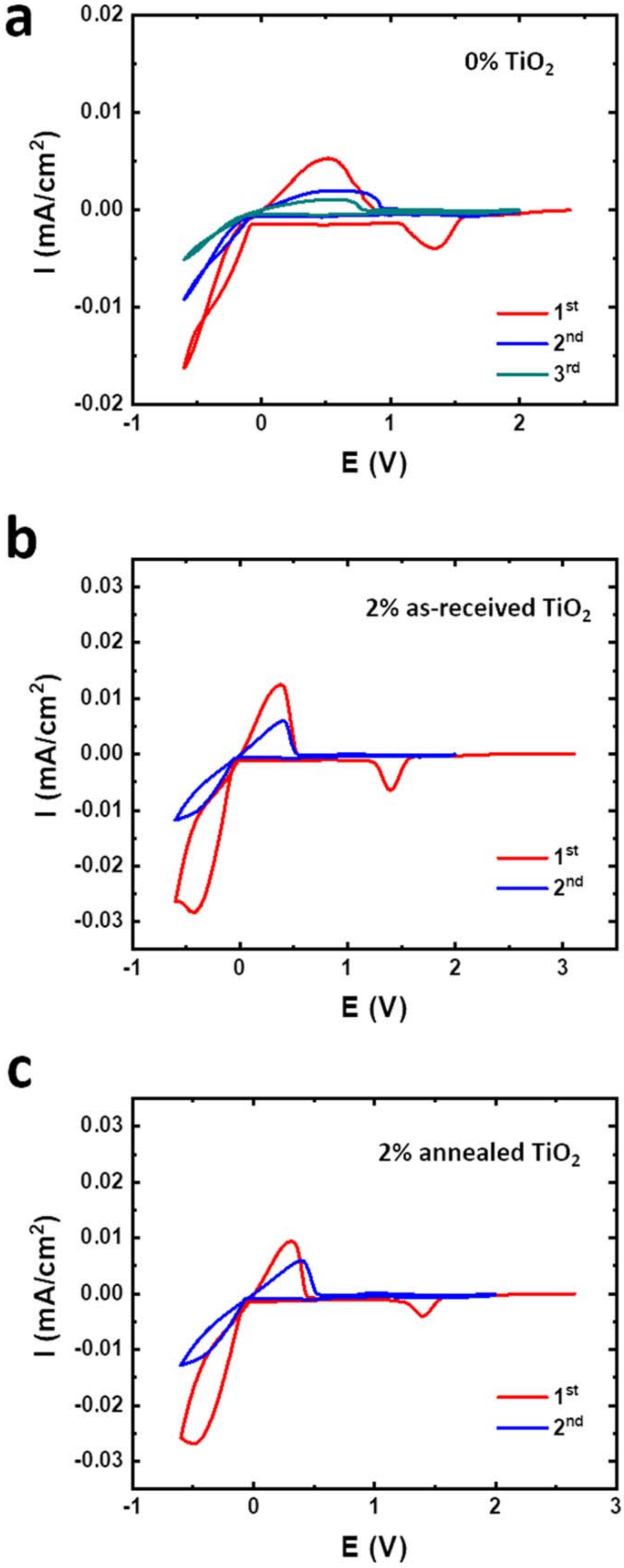

Figure 2. Cyclic voltammetry of Li/stainless-steel cells with (a) PVdF-HFP/$LiClO_4$, (b) PVdF-HFP/$LiClO_4$/as-received-TiO_2. (c) PVdF-HFP/$LiClO_4$/annealed-TiO_2 solid polymer electrolytes.

annealed-TiO_2 sample is about 18% lower than that of the as-received TiO_2 sample. Note that the amount of salt, polymer, and the TiO_2 nanoparticles are identical in both the systems and that the difference only lies in the fact that the TiO_2 particles were annealed in the former sample. The fact that the charge transferred in the as-received sample is higher denotes that there were additional charge carriers present in it, and therefore serves as a direct evidence of the enhancement in conductivity observed in the as-received sample.

Figure 3a shows the comparison of conductivities of the SPEs annealed-TiO_2 and as-received-TiO_2 nanoparticles in the temperature range of 10 °C − 80 °C. The SPE with as-received-TiO_2 fillers exhibit higher conductivities at all temperatures owing to the presence of the surface protons and –OH groups and the resulting additional conductivity. Since the impedance spectroscopy tests carried out in a blocking electrode set-up does not distinguish the type of ions involved in the conduction, the contribution from the surficial groups shows as an increase in the overall conductivity. However, to confirm that this annealing step is not detrimental to functioning of the solid polymer electrolyte, its lithium/plating stripping behavior needs to be investigated for several cycles. In this context, galvanostatic cycling was carried out with symmetric Li–Li cells with the SPE sample with annealed-TiO_2 nanoparticle fillers. The occurrence of smooth plating/stripping profiles is typically considered as evidence of an electrolyte to successfully transport Li^+ ions. Figure 3b shows the plating/stripping profiles and the deposition overpotentials obtained for 100 h. The potentials shown in the plots are normalized by thickness, and the raw data are provided in Figs. S4–S5 and Table SI of Supporting Information. The uniform voltage profiles in Fig. 3b indicate that the SPE with 2% annealed-TiO_2 nanoparticle fillers can plate/strip Li for up to 100 h. Figure 3c shows the representative cycles between 40–45 h. The low overpotentials of $15\,\mathrm{mV}\,\mu\mathrm{m}^{-1}$ indicate the efficient deposition of Li^+ ions onto Li metal electrodes. Therefore, despite the reduction in conductivity upon annealing the ceramic nanoparticle fillers, the SPE can indeed plate/strip Li successfully.

In contrast, the cell with the ceramic-free electrolyte, i.e., PVdF-HFP/$LiClO_4$ polymer electrolyte without TiO_2 nanoparticles, showed stable cycling only for about 1.1 h (Fig. S2, Supporting Information), after which it showed a sharp jump in the overpotential and an immediate decrease to potentials even lower than the annealed-TiO_2 sample. Typically, such a sharp reduction in the overpotentials is attributed to short circuiting due to dendritic growth, and has been well documented in the previous literature reports.[19,23] The Nyquist plot of this symmetric cell showing the interfacial resistance is provided in Fig. S3, Supporting Information. It has earlier been shown that the addition of TiO_2 nanoparticles to polystyrene-block-poly(ethyleneoxide)-based polymer electrolytes improves the mechanical properties of the polymer films and prolongs the life of symmetric cells.[19] Our observation that the symmetric cell with TiO_2 nanoparticles performs better indicates that this effect is also applicable to our PVdF-HFP-based system. Although the low-conductivity ceramic-free SPE performed poorly, the conductivity is generally not a good indicator of the observed potentials. The relationship between the current density and potential profiles is considered non-linear in nature with their dependence also related to other factors such as salt concentrations and current densities.[24] Nevertheless, this comparison of conductivities of annealed-TiO_2 and as-received-TiO_2 samples demonstrates the importance of annealing the nanoparticle fillers before adding them to the polymer electrolyte to obtain the true enhancement in Li^+ conductivity.

Conclusions

PVdF-based solid polymer electrolytes with added TiO_2 nanoparticle fillers have been developed for application in Li-metal batteries. To isolate the enhancement due to surface adsorbed moisture and proton groups, a sample with annealed TiO_2 nanoparticles was prepared and its performance was compared with that of the as-received TiO_2 nanoparticles. Interestingly, a reduction in conductivity was observed in the annealed-TiO_2 samples, which

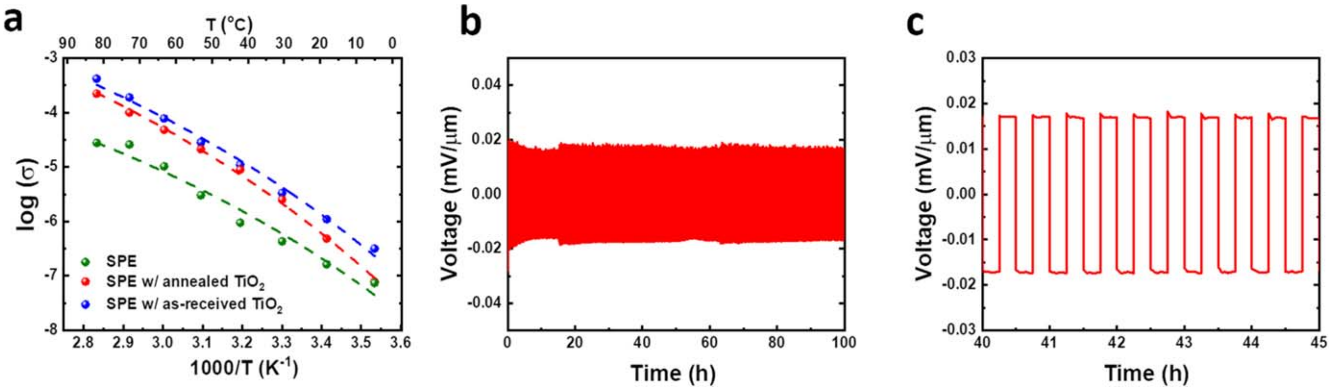

Figure 3. (a) Comparison of the ionic conductivities of PVdF-HFP/$LiClO_4$ solid polymer electrolyte (SPE) and the SPEs with 2% as-received-TiO_2 and 2% annealed-TiO_2 in the temperature range 10 °C–80 °C. The dotted lines represent the Vogel-Tammann-Fulcher (VTF) fits for all the datasets. (b) Galvanostatic cycling profile of the symmetric Li | Li cell with the PVdF-HFP/$LiClO_4$ polymer electrolyte with 2% annealed TiO_2, showing the potentials normalized by thickness. The cycling test was carried out at a current density of 0.05 mA cm^{-2}. (c) Representative cycles between 40−45 h in the galvanostatic cycling test in (b), showing smooth Li plating/stripping profiles.

indicates that the additional conductivity obtained in as-received TiO_2 sample could have possibly originated from species that were removed during the annealing step, i.e., surface adsorbed moisture/protonic groups. To ascertain the plating/stripping behavior of the composite polymer electrolyte with TiO_2 nanoparticles, galvanostatic cycling of the Li/Li symmetric cells were conducted. Low plating/stripping overpotentials of 10–20 mV were observed for 100 cycles, which indicates the efficient deposition of Li^+ ions onto Li metal electrodes. Nevertheless, we emphasize the need to anneal the ceramic nanoparticle fillers prior to their incorporation in solid polymer electrolytes to obtain a true enhancement in Li^+ conductivity.

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