Interfacial engineering of lithium-polymer batteries with in situ UV cross-linking

Ramin Rojaee1 | Samuel Plunkett2,3 | Md Golam Rasul1 | Meng Cheng1 | Vahid Jabbari1 | Reza Shahbazian-Yassar1

1Mechanical and Industrial Engineering Department, University of Illinois at Chicago, Chicago, Illinois, USA
2Materials Science Division, Argonne National Laboratory, Lemont, Illinois, USA
3Department of Chemical Engineering, University of Illinois at Chicago, Chicago, Illinois, USA

Correspondence
Reza Shahbazian-Yassar, Mechanical and Industrial Engineering Department, University of Illinois at Chicago, Chicago, IL 60607.
Email: rsyassar@uic.edu

Funding information
National science foundation, Grant/Award Number: CBET-1805938;
Northwestern University; University of Illinois at Chicago

Abstract
Developing promising solid-state Li batteries with capabilities of high current densities have been a major challenge partly due to large interfacial resistance across the electrode/electrolyte interfaces. This work represents an integrated network of self-standing polymer electrolyte and active electrode materials with in situ UV cross-linking. This method provides a uniform morphology of composite polymer electrolyte with low thickness of 20–40 μm. This modification leads to promising cycling results with 85% specific capacity retention in Li||LiFePO4 cell over 100 cycles at high current densities of 170 mA g−1 (≈25 μA cm−2, 1 C). By applying this method, the interfacial resistance decreases as high as seven folds compared to noncross-linked interfaces. The following work introduce a facile and cost-effective method in developing fast-charging self-standing polymer batteries with enhanced electrochemical properties.

KEYWORDS
electrochemical impedance spectroscopy, interfacial engineering, lithium batteries, self-standing polymer electrolyte

INTRODUCTION

Solid-state Li+ ion batteries offer safe, lightweight, and high energy batteries due to the use of Li metal as anode.1-3 Organic polymer gels or inorganic solid-state electrolytes can improve the electrochemical performance due to their high inherent mechanical properties that can effectively block the dendrite growth.4-7 They also offer high safety applications with no liquid leakage.8 The widely investigated inorganic solid-state electrolytes including Li10GeP2S12 (LGPS), Li3PO4Nz (LiPON), or LISICON (Li1+3Si1−xXxO4 [X = P, Al, or Ge]) often require complicated and expensive processability such as high temperature synthesis and extra pressure loads.9-12 Moreover, poor Li+ ion conductivity at the bulk electrolyte and the electrode/electrolyte interface is the major bottleneck of solid-state batteries for large-scale applications.13 Solid-state electrolytes often demonstrate poor performance in long cycle life and high current densities, owing to large interfacial voltage polarizations.14 This large voltage polarization is due to kinetic limitation of Li+ ions through the electrolyte, loose electrode/electrolyte interfacial contact, and sluggish diffusivity at the interfaces.15

There have been extensive efforts to address the electrode/electrolyte interfacial issues in solid-state
Electrolytes. Elevating operational temperatures have shown to improve diffusivity of Li$^+$ ions through the bulk electrolyte and lowers the interfacial resistance$^{16}$. However, it is important to note that the increased working temperature of the Li$^+$ ion batteries can accelerate aging and potentially trigger thermal runaway.$^{17-19}$ An alternative approach to enhance the electrode/electrolyte interfacial stability is solid–liquid hybrid electrolyte. In these batteries, the liquid phase infuses through the electrode pores and promotes the interfacial dynamics. This phenomenon improves the cyclability and charging current density of such batteries at room temperature.$^{20,21}$ However, the hybrid solid/liquid electrolytes can potentially lead to safety issues due to the presence of liquid phase. Artificial coating at the electrode/electrolyte interface is another process to improve the contact and increase the Li$^+$ ion flux at the interface.$^{22,23}$ Chen et al.$^{24}$ developed a solid-state battery with poly(propylene carbonate)-based polymer electrolyte. A coating of graphite layer was performed at the anode/electrolyte and cathode/electrolyte. They showed that this layer acts as a buffer layer at electrode/electrolyte interface, which decreases the interfacial resistance and blocks the propagation of lithium dendrites.$^{24}$ However, this method adds more complexity to the production of such batteries.

One way to improve the interfacial properties is to mix a fraction of solid electrolyte with cathode slurry, known as catholyte. Catholyte provides an integrated network of electrolyte/cathode active materials and lowers the activation energy for Li$^+$ ions transport.$^{25,26}$ Although this method improves the electrode/electrolyte interfacial contact, it reduces the electrical properties of the electrodes. In addition, the idea of using catholyte could not effectively reduce the voltage polarization since the reported volume fraction of electrolyte is often in a very high range of 30–40 vol%.$^{27}$ Therefore, moderate electrochemical performance of solid-state electrolytes by using catholyte was only reported at elevated temperatures of $>60^\circ$C.$^{28,29}$ In addition, large volume fraction of inactive materials in the catholyte reduces the specific energy and power density of the battery. However, the idea of using catholyte is relatively new and has the potential to enhance the electrochemical properties of solid-state batteries.

Combining the merits of organic polymer materials for introducing mechanically robust electrolytes$^{30}$ and catholytes, we utilized the electrolyte that was developed by Porcarelli et al.$^{31}$ and engineered an in situ UV cross-linking of the integrated composite polymer electrolyte (CPE) and the cathode active materials. The degree of cross-linking was measured to be $\sim$58%, which is enough to be flexible self-standing electrolyte film with good adhesion properties. The current method uses $<5$ vol% of electrolyte as part of catholyte and results in an intact interfacial contact. In addition, this process offers a very low electrolyte thickness of 20–40 μm. We showed that this process effectively reduces the electrolyte/cathode interfacial resistance up to 700% and significantly increases the cyclability of such batteries at high current densities of up to 170 mA g$^{-1}$ ($\sim$25 μA cm$^{-2}$).

2 | RESULTS AND DISCUSSION

Figure 1 shows a schematic illustration of a conventional preparation of solid polymer electrolyte (Figure 1 (A)) compared to integrated UV-triggered synthesis method (Figure 1(B)). The conventional preparation of self-standing polymer battery cannot provide a reliable contact between the active material’s particles and the electrolyte and leads to large resistance at the interface.$^{32}$ In addition, electrode particles cannot be soaked thoroughly with this electrolyte. Therefore, part of electrode active materials’ mass would not participate in electrochemical interactions, leading to large overpotential values for transporting Li$^+$ ions.$^{33}$ The large overpotential accelerates undesired side reactions and results in degradation of battery materials.$^{34}$ The proposed solution to minimize the abovementioned challenges is to develop an integrated electrode/electrolyte structure as shown in Figure 1(B). To acquire such structure, the cathode slurry was mixed with tetraethylene glycol dimethyl ether (TEGDME) as a cross-linking agent and benzophenone photo-initiator. This leads to a coverage of nearly all the active material particles and provides a perfect interfacial contact upon UV stimulation. More details are provided in the experimental section.

It is well known that the electrolyte thickness determines the diffusion length of Li$^+$ ions. Therefore, controlling the electrolyte thickness is important to achieve better electrochemical performance.$^{35}$

Figure S1 compares the SEM cross-sectional images of conventional self-standing polymer electrolyte in the presence of cathode laminate and in situ UV integrated electrode/electrolyte. As demonstrated in Figures S1(a), the conventional polymer electrolyte is segregated from the cathode laminate with a distinguished boundary. This observation shows a poor electrolyte adhesion of conventional electrolyte at the electrode/electrolyte interface. However, the in situ cross-linked CPE could infuse and bond with the electrode laminate very efficiently with no distinguishable interface (Figure S1(b)). Figure 2 shows the scanning electron microscopy (SEM) cross-sectional image of the developed catholyte and the corresponding energy dispersive X-ray spectroscopy
(EDS) elemental distribution mapping of this region. As can be clearly seen, the in situ of electrode/electrolyte method allows a thin electrolyte coating (20–40 μm). In addition, the SEM image shows that the electrolyte is well diffused through the cathode particles. The in situ UV cross-linking of electrolyte through the cathode laminate creates an integrated electrode-electrolyte layers and enhances interfacial ionic conductivity. This is expected to lead to decrease in interfacial resistance and to improve the utilization of cathode active materials. Different layers of this cross section can be identified easily via EDS mapping. Since the cathode is laminated on aluminum (Al) foil, a strong signal of Al is observed. Phosphorus (P) and iron (Fe) signals, however, are only present in the cathode active material (LiFePO₄). Moreover, the only source of sulfur (S) signal is resulting from the Li-salt (LiTFSI) and ionic liquid (EMIM-TFSI) precursors as two main electrolyte components. Interestingly, the S map shows that the electrolyte is well dispersed through the electrode pores,
resulting a perfect integrity at electrode/electrolyte interface.

In the next step, the impedance behavior in the in situ cross-linked cells was studied. For this purpose, we utilized electrochemical impedance spectroscopy (EIS), which is a powerful tool to study the bulk ionic conductivity of the electrolyte and analyzing electrode/electrolyte interfacial resistance. The resulting equivalent electrical circuit can distinguish the resistive behaviors of the battery components at different frequencies. Figure 3 shows the experimental and simulation EIS analyses of the conventional and in situ UV cross-linked self-standing polymer batteries before cycling. The simulated graph is plotted with the closest equivalent circuit values to the corresponding experiment. The resistive behavior of the bulk electrolyte can be measured from Nyquist plot via the intercept of first green-colored circle with the X-axis (Re(z)). In the conventional method, the bulk electrolyte shows an average resistance of 129 Ω and average ionic conductivity $2.7 \times 10^{-4}$ S cm$^{-1}$. The detail of this calculation can be found in experimental section. For the in situ UV cross-linked method, however, the bulk electrolyte resistance is showing a value of 20 Ω, resulting an ionic conductivity of $5.3 \times 10^{-4}$ S cm$^{-1}$. It is worth noting that the transference number of the CPE was measured to be about 0.1. The details of this measurement are explained in the experimental section and Figures S2.

Ionic conductivity of the developed CPE was measured as a function of temperature in Figure S3. It should be noted that the transference number and bulk ionic conductivity of the two samples are not expected to show huge difference, since the composition of the electrolytes are similar. However, the slight enhancement in bulk ionic conductivity of in situ UV cross-linked method (Figure 3) is due to the better structural integrity of the electrolyte. As shown in Figure 3, three different time-constants of two charge-transfer resistive behavior and one semi-infinite diffusion can be observed in the EIS spectra of both samples. These phenomena are related to different charge-transport processes through solid–electrolyte interphase (SEI), electrolyte, anode, and cathode active materials. It should be noted that these processes are usually subtle and distinction of impedance ranges for the individual transfer processes is complicated. In order to simplify the analysis, the ionic resistance of the bulk electrolyte is modeled with a resistor (R) followed by three parallel resistor and nonideal capacitor (Q) model for each charge-transfer process. The relative semi-circles were fitted at each frequency range to the experimental graph according to simulated electrical circuits. As marked in Figure 3, the first resistive behavior starting at 628 kHz could be related to formation of solid electrolyte interphase (SEI) and charge-transfer resistance at Li/CPE. These resistances demonstrate values of 129 Ω and 20 Ω, respectively.
146 and 137 Ω for conventional and in situ UV cross-linked CPEs, respectively. Since no specific interfacial enhancements have been performed at the anodic (Li/CPE) interface, these values are roughly similar for both samples. It is worth noting that the time-constant starting at 46 and 3 Hz (marked in Figure 3(A,B)) for conventional and in situ cross-linking electrolyte is related to diffusion-limited processes of Li\(^+\) ions within the electrode particles. These diffusion processes are mainly associated with physical and chemical properties of the active material such as active material's composition and particle size.\(^{31-43}\) Since no changes have been performed on these properties, the variations of this behavior are subtle and are not studied in this work. The time-constant centering at 167 and 132 Hz (marked in Figure 3(A,B)) is attributed to charge-transfer resistance of Li\(^+\) ions at CPE/LiFePO\(_4\) interface.\(^{38,44}\) The geometry of electrode/electrolyte contact is one of the major parameters that is involved in changing this resistance.\(^{45}\) The interfacial resistance values of CPE/LiFePO\(_4\) is measured to be 325 Ω for in situ cross-linked cell. This is ~30% lower than its counterpart interfacial resistance of the conventional method with the value of 447 Ω. This reduction in interfacial resistance is due to the inter-connected design of the cathode particles and the electrolyte, which results in more facile ion-transfer through the CPE/LiFePO\(_4\) interface. Moreover, since all the active material particles are surrounded by the electrolyte in in situ cross-linking technique, the designed catholyte is able to offer a better capacity (closer to the theoretical capacity of the electrode material) unlike the conventional cell.

In order to capture a real-time effect of interfacial engineering on the electrode/electrolyte resistance, the EIS plots have been monitored after each charge/discharge in a course of 100 cycles at current density of 0.2 C. Figure 4 shows the Nyquist plots of the conventional and in-situ cross-linked CPE after charge and discharge at 5, 10, 20, 40, 60, 80, 100 cycles. As shown in Figure 4(A,B), no significant changes can be observed for bulk electrolyte resistance and CPE/Li interfacial resistance over cycling. This shows that the CPE has high electrochemical stability and compatibility with the Li metal while cycling. Since the interfacial engineering has been only performed on the cathode side in the Li\|LiFePO\(_4\) half-cell, we focus on the charge-transfer resistance at CPE/ LiFePO\(_4\) interface. In general, the resistance increases due to formation of insulative layer at the interface during cycling.\(^{46}\) Interestingly, the CPE/LiFePO\(_4\) of in situ cross-linking method shows a very stable resistance value and barely exceeds 1000 Ω. However, the CPE/LiFePO\(_4\) resistance shows a large value of ranging 5500–7050 Ω for conventional CPE. The 500%–700% reduction of CPE/LiFePO\(_4\) resistance can
significantly change the electrochemical performance of the self-standing polymer battery.

Figure 4(C) demonstrates a comparison graph of CPE/LiFePO4 versus cycle number in both cells after each charge. As shown in Figure 4(C), the in situ cross-linked CPE showed stable resistance values for the first 40 cycles with the average resistance of 795 ± 40 Ω. The resistance of in situ cross-linked CPE increased with a moderate slope to the average value of 1000 ± 100 Ω over 100 cycles. However, the conventional CPE experienced over a 10% increase in resistance from Cycle 5 to Cycle 10. Although conventional CPE showed a relatively stable resistance of 6360 ± 10 Ω from cycle 20 to 60, it is yet >700% of the resistance values in in situ cross-linked CPE. This interfacial resistance increased to over 7000 Ω for conventional CPE after 100 cycles, indicating the sluggish Li+ ion flux at the interface. It is worth noting that in conventional method, there is a poor contact at electrode/electrolyte interface. By applying voltage, huge overpotential forms against lithium ion transfer which can lead to increased side reactions and formation of insulative products at the interfaces. As a result, the resistance shows increased values even after few cycles and can explain the different EIS behavior of this sample.

In order to study the cyclability of the in situ cross-linked electrolyte, the electrochemical stability and voltage polarization of the CPE were investigated. Figure 5 (A) demonstrates the voltage stability window of ca. 5 V versus Li/Li+ for the developed CPE. This wide electrochemical window is reported in other studies as well and is related to the oxidation decomposition of electrolyte composite at higher voltages.31,47 Figure 5(B–F) depicts the overpotential values of symmetric Li||Li cells at different current densities of 5–50 μA cm−2. Low overpotential values of this CPE at 5–15 μA cm−2 with the highest value of ca. 180 mV versus Li/Li+ show promising electrochemical stability of bulk electrolyte over 1000 charge–discharge cycles at low-current densities. While, the overpotential values of this electrochemical cell increases to highest values of ca. 310 and 405 mV at higher current densities of 20 and 50 μA cm−2, respectively, the voltage polarization remains nearly stable over the course of 1000 cycles. This indicates a stable electrochemical behavior of such CPEs. It is also important to note that no short-circuit was observed in these voltage polarization profiles. It indicates that the CPE provided a safe operation and could block the lithium dendrite penetration over long cycles.31,48

Studying the voltage profile of the developed battery can determine the cyclability and electrochemical robustness of such cells after interfacial engineering. Figure 6 compares the long-term cycling performances of the conventional and in situ cross-linked CPEs within 100 cycles at high current densities of 1 C (~25 μA cm−2, 170 mA g−1) between 2.5 and 4.2 V versus Li/Li+. As can be seen in Figure 6(A,B), the conventional CPEs have a poor initial specific discharge capacity of 31 mAh g−1, which degrades to 4 mAh g−1 over the course of 100 cycles. In addition, this cell experiences a low Coulombic efficiency of ~82% which is mainly due to high overpotential values. The fast capacity decay in conventional cell configuration is related to huge increase in electrode/electrolyte interfacial resistance by cycling as discussed in Figure 4. The poor contact between electrode and electrolyte materials are originating from nonsimilar materials, which can be further exacerbated due to volume changes during cycling.49 This is in agreement with previous observation by Kaneko et al.50 where they reported a gradient of Li+ ion salt concentration and Li+ ion depletion in their developed cell. This phenomenon which occurs at relatively high discharge rates, is responsible for undesirable side reaction at the interface and limiting the electrochemical performance.50,51 Figure S6 compares the surface morphology of Li metals for conventional CPE and the in situ cross-linked CPE after long cycling. As shown in Figure S7, the conventional CPE cell configurations are more prone to form dendrites due to high interfacial impedance and more active side reactions. On the other hand, the initial specific discharge capacity of in situ cross-linked CPE is measured to be 133 mAh g−1. As shown in Figure 6(C), this cell represents a high capacity retention of ca. 85% (of initial capacity) after 100 cycles (113 mAh g−1). Interestingly, the Coulombic efficiency of this cell remains at steady average value of ca. 98.5 ± 1%. This shows a great electrochemical stability of such cells, making it viable for long cycle life. It should be noted this great electrochemical performance at nearly room temperature (35°C) is not reported in other studies. In a study by Gutiérrez-Pardo et al.25 and Martinez et al.,27 mixing poly(ethylene oxide) (PEO)-based composite polymer electrolyte with LiFePO4 could demonstrate enhanced electrochemical properties at 70°C at current densities of 0.05–0.5 C. However, their battery showed more than 90% capacity reduction. In our study, although the voltage polarization of this battery slightly increases from 150 mV at the first cycle to 360 mV at 100th cycle, it is still showing a high specific discharge capacity of 113 mAh g−1 by 100th cycle.

In summary, the in situ cross-linking of electrolyte provides an integrated network of electrode/electrolyte structure, which significantly improves the interfacial contact and enhances the accessible capacity of the cathode. This novel method not only offers stable electrochemical properties but also plays a significant role to increase the charging rate of self-standing polymer batteries. Further studies can be considered to increase the mass loading of cathode and study the electrochemical
FIGURE 5  Electrochemical stability and cyclability of the developed SSE. (A) Plot of current versus working potential (vs. Li/Li$^+$) showing the electrochemical voltage stability window. (B) Plot of voltage polarization versus time at (B) 5 μA cm$^{-2}$, (C) 10 μA cm$^{-2}$, (D) 15 μA cm$^{-2}$, (E) 20 μA cm$^{-2}$, and (F) 50 μA cm$^{-2}$
properties of such batteries at different cycling and environmental conditions.

3 | CONCLUSIONS

In conclusion, the in situ UV cross-linking of the electrolyte and electrode materials provides a well-integrated network for the Li\(^{+}\) ion flux in self-standing polymer batteries. The present method has led up to 700% reduction in interfacial resistance of CPE/LiFePO\(_4\) cells after 100 cycles. The in situ UV cross-linking method reduced the amount of electrolyte usage within the catholyte composite to as low as 5 vol%. Stable cycling performance with outstanding capacity retention of >110 mAh g\(^{-1}\) was achieved after 100 cycles at high current densities 1 C (170 mA g\(^{-1}\)). This interfacial engineering technique potentially increase gravimetric and volumetric energy densities and facilitates sustainable high performance self-standing polymer lithium batteries.

**Experimental section**

The 20 wt% of tetraethylene glycol dimethyl ether (TEGDME, Sigma Aldrich), 20 wt% of poly(ethylene oxide) with the average molecular weight of 100 000 g mol\(^{-1}\) (PEO, Sigma-Aldrich) were mixed onto a hot plate (IKA, 381000X) at 80°C and 50–80 rpm. The 30 wt% of bis(trifluoromethylsulfonyl)imide (EMIM-TFSI, Iolitec), and 5 wt% of benzophenone (Alfa Aesar) were mixed together in a separate container and mixed onto a hot plate at 60–80°C and 100–150 rpm for at least 2 h until a clear solution was achieved. Afterward, all the solutions were added together mixed onto a hot plate at 60–80°C and 160 rpm for about 12 h. This time let the solution disperse the precursors uniformly and undergo chemical reactions for processing co-polymer electrolyte nanocomposite.

The cathode laminate was made with lithium iron phosphate (LiFePO\(_4\)) as the active material. To produce in situ cross-linked self-standing polymer batteries, the cathode slurry was made upon rigorous mixing of 60 wt % of active material, 25 wt% of carbon black, Super P® Conductive (Alfa Aesar) and 10 wt% of poly(vinylidene fluoride) as binder in adequate amount of 1-methyl-2-pyrrolidinone solvent. Two main electrolyte components of 2 wt% of benzophenone (Alfa Aesar) and 10 wt% of poly(vinylidene fluoride) as binder in adequate amount of 1-methyl-2-pyrrolidinone solvent. Two main electrolyte components of 2 wt% of benzophenone (Alfa Aesar) and 10 wt% of tetraethylene glycol dimethyl ether (Sigma Aldrich) were also mixed in the cathode slurry. The slurry was then coated on battery grade aluminum foil (MTI, 20 μm thickness) using doctor blade technique. The cathodes were then dried in a vacuum oven at 70°C for 24 h to remove the residual solvent traces (if any). The same procedure was used to prepare cathode laminates for conventional self-standing polymer battery production with the cathode slurry including 60 wt% of active material, 25 wt% of carbon black, Super P® Conductive (Alfa Aesar) and 15 wt% of poly(vinylidene fluoride) as binder in adequate amount of 1-methyl-2-pyrrolidinone solvent.
In order to produce in situ cross-linked self-standing polymer cells, the co-polymer electrolyte nanocomposite electrolyte was then dispersed on the cathode laminates at 60°C. This temperature allows the gel to diffuse through the cathode laminate pores. The resulting electrolyte/cathode laminate layer was exposed to UV light of 100 mW cm\(^{-2}\) for 20 min in a closed mirrored box. A firm and flexible integrated self-standing polymer electrolyte (20–40 μm) and catholyte forms at this stage. The Li metal chips were then wetted with the electrolyte on one surface and placed on top of the integrated electrolyte and catholyte. The sandwiched structure was again exposed to UV light for 10 min to provide a reliable contact at the interfaces. For conventional solid-state batteries, however, the co-polymer electrolyte nanocomposite electrolyte was poured on a glass slide at 60°C and irradiated under UV light of same abovementioned power for 30 min. The resulting self-standing polymer electrolyte was then peeled off from the substrate and put on the cathode laminate with a thickness of roughly 100 μm.

X-ray diffraction (XRD) measurements were performed at ambient temperature on a STOE-STADI-P diffractometer equipped with an asymmetric curved Germanium monochromator (CuKα1 radiation, \(\lambda = 0.154056\) nm) and one-dimensional silicon strip detector (MYTHEN2 1K from DECTRIS). The instrument was calibrated against a NIST Silicon standard (640d). The line-focused Cu X-ray tube was operated at 40 kV and 40 mA. The scans were collected for the 2θ = 5°–80° at the rate of 0.015° min\(^{-1}\).

Differential scanning calorimetry (DSC) measurements were performed by using Discovery DSC 2500 (TA instrument, Inc.). The samples were heated from room temperature to 125°C with the heating rate of 10°C min\(^{-1}\). The samples were then held at 125°C for 5 min under N\(_2\) gases to remove the thermal hysteresis. Next, the samples were cooled down with the cooling rate of 10°C min\(^{-1}\) to −85°C and held for 5 min. Finally, they were heated to 125°C with similar heating rate as before. The degree of crystallinity (\(X_c\%\)) of the electrolyte was calculated by performing DSC by using the following equation\(^{52,53}\):

\[
X_c\% = \frac{\Delta H_{\text{m}}}{(W \times \Delta H_{100\%})} \times 100\% \tag{1}
\]

where \(\Delta H_{\text{m}}\) (J g\(^{-1}\)) is the latent heat of fusion of the sample, \(W\) is the weight fraction of PEO in the sample, and \(\Delta H_{100\%}\) (J g\(^{-1}\)) is the theoretical latent heat of fusion for 100% crystalline PEO. Figure S5 shows the details of this calculation.

The degree of a cross-linkable polymer matrix is calculated using following equation\(^{54}\):

\[
D = \left(\frac{m}{m_0}\right) \times 100 \tag{2}
\]

where \(m_0\) and \(m\) are the initial weight of polymer film and after removing the soaking solvent (dried sample).

To measure \(D\), a polymer electrolyte film with a known weight (\(m_0 \sim 0.2\) g) is swollen by acetonitrile solvent for at least 24 h. This solvent dissolve the non-crosslinked polymer segments leaving only the crosslinked polymer parts. The swollen film is isolated from the liquid medium and dried at 90°C for 24 h to remove solvent residuals. Finally, the film is weighted to measure \(m\) (≈0.125 g) and calculate \(D\).

Hitachi S-3000 N and a built-in EDS (Oxford Inca, 15 mm WD) was used for imaging the morphology and elemental map of the samples. Further SEM images of the surface morphology of samples was studied by the JEOL JSM-IT500HR SEM. The images were acquired at an acceleration voltage of 5 kV.

Electrochemical tests were conducted using either BioLogic VMP3 potentiostat, Neware CT-4008 battery cyclers. All electrochemical experiments including linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), and cycling tests were performed at 35°C if not specifically stated.

The cells were assembled using CR2032-type coin cell (MTI corporation) by coating the cathode laminate and Li-metal anode with developed solid polymer electrolyte at 80°C. The thickness of the electrolyte was controlled to be in similar range by adding 500 mg of electrolyte to the coin cell designs. The electrode configurations varied for different electrochemical tests. All the cell assembly processes were performed in an argon-filled glovebox (MBraun Labstar, O\(_2\) and H\(_2\)O content <1 ppm) filled with ultra-high purity Ar gas.

Galvanostatic charge/discharge cycling tests were carried out by using half-cell setup of LFP (cathode) and Li metal (anode and reference) electrodes (Li||CPE||LFP) in the potential range of 2.5–4.2 V versus Li/Li\(^+\) at various C-rates, where the 1 C rate corresponds to a current density of 170 mAh g\(^{-1}\). The current density was \(~170\) mA g\(^{-1}\) (\(~25\) μA cm\(^{-2}\)) for 1 C. Cathode loading is in average 2.71 mg cm\(^{-2}\) (60 wt% active material). The surface area of the coin cell-cut cathode laminate is \(~2.84\) cm\(^2\). The cells were left at open circuit voltage for 12 h before test. The very initial charge/discharge cycles are attributed to the SEI formation processes, as usual in standard cell manufacturing.\(^{55}\)

The time evolution of voltage profiles was performed on symmetric Li||CPE||Li cells under constant current densities of 5, 10, 15, 20, and 50 μA cm\(^{-2}\). The test followed by a 0.5 h discharge and 0.5 h charge for each cycle up to 1000 h.

Electrochemical stability of the electrolytes was obtained by linear sweep voltammetry using stainless-
steel (St.St.) as the working electrode and a lithium disk as the counter and reference electrodes (Li||CPE||St.St.). The linear sweep voltammograms were recorded between 2 and 6 V (vs. Li/Li⁺) at a scan rate of 0.5 mV s⁻¹.

The bulk electrolyte ionic conductivities were measured by electrochemical impedance spectroscopy (EIS) analysis using Li||CPE||LiFePO₄ cells between 10 and 1 MHz with zero applied potential at sinus amplitude of 10 mV at 35°C. EIS spectra were also used to analyze the electrode/electrolyte interfacial resistance in symmetric Li||CPE||LiFePO₄ cells before and after long-term cycling. The built-in electrical circuit simulation tool of Biologic® (Z-fit or Z-Sim) was used to evaluate the CPE||LiFePO₄ resistance.

The bulk resistance of the samples was calculated from the intercept of impedance curve and the x-axis (Re (Z)) value. The ionic conductivity was calculated by the following equation:

\[ \sigma = \frac{L}{R_b \cdot S} \]  

where \( \sigma \) is the ionic conductivity (S cm⁻¹), \( R_b \) is the bulk resistance (Ω), \( L \) is the distance between the two working and counter electrodes, which is the thickness of the electrolyte (cm), and \( S \) is the surface area of the working electrode (cm²).

The transference number (\( t_+ \)) was measured by monitoring impedance values before and after the chronamperometry measurements of symmetric Li||Li cells at small voltage polarization (\( \Delta V = 10 \) mV). Equation (4) was used to calculate the \( t_+ \):

\[ t_+ = \frac{I_{SS}(\Delta V - I_0 R_b)}{I_0(\Delta V - I_{SS} R_{SS})} \]  

where \( \Delta V \), \( I_0 \), \( I_{SS} \), \( R_b \), \( R_{SS} \) is the applied potential, initial perturbation current, steady-state current, real-value of impedance before the polarization, and real-value of impedance after polarization, respectively.

ACKNOWLEDGMENTS
This experimental work is financially supported by the NSF Award number CBET-1805938. The authors acknowledge the characterization facilities provided by University of Illinois at Chicago, Research Resources Center, Electron Microscopy Core and KECK-II facilities of Northwestern University's NUANCE Center.

REFERENCES
1. Zhang H, Li C, Piszcz M, et al. Single lithium-ion conducting solid polymer electrolytes: advances and perspectives. Chem Soc Rev. 2017;46(3):797-815.
2. Zhang Z, Antonio RG, Choy KL. Boron nitride enhanced polymer/salt hybrid electrolytes for all-solid-state lithium ion batteries. J Power Sources. 2019;435:226736.
3. Cui Y, Wan J, Ye Y, Liu K, Chou LY, Cui Y. A fireproof, lightweight, polymer-polymer solid-state electrolyte for safe lithium batteries. Nano Lett. 2020;20(3):1686-1692.
4. Liu H, Cheng XB, Huang JQ, et al. Controlling dendrite growth in solid-state electrolytes. ACS Energy Lett. 2020;5(3):833-843.
5. Tikekar MD, Choudhury S, Tu Z, Archer LA. Design principles for electrolytes and interfaces for stable lithium-metal batteries. Nat Energy. 2016;1(9):1-7.
6. Zhao Q, Stalin S, Zhao CZ, Archer LA. Designing solid-state electrolytes for safe, energy-dense batteries. Nat Rev Mater. 2020;5(3):229-252.
7. Liu FQ, Wang WP, Yin YX, et al. Upgrading traditional liquid electrolyte via in situ gelation for future lithium metal batteries. Sci Adv. 2018;4(10):1-10.
8. Liang Y, Zhao C, Yuan H, et al. A review of rechargeable batteries for portable electronic devices. InfoMat. 2019;1(1):6-32.
9. Mauger A, Julien CM, Paolella A, Armand M, Zaghib K. Building better batteries in the solid state: a review. Materials (Basel). 2019;12(3):1-86.
10. Kobayashi T, Yamada A, Kanno R. Interfacial reactions at electrode/electrolyte boundary in all-solid-state lithium battery using inorganic solid electrolyte, thio-LISICON. Electrochim Acta. 2008;53(15):5045-5050.
11. Bachman JC, Muy S, Grimaud A, et al. Inorganic solid-state electrolytes for lithium batteries: mechanisms and properties governing ion conduction. Chem Rev. 2016;116(1):140-162.
12. Deng Y, Eames C, Fleutot B, et al. Enhancing the lithium ion conductivity in lithium superionic conductor (LISICON) solid electrolytes through a mixed polyanion effect. ACS Appl Mater Interfaces. 2017;9(8):7050-7058.
13. Yu C, Ganapathy S, Eck ERHV, et al. Accessing the bottleneck in all-solid state batteries, lithium-ion transport over the solid-electrolyte-electrode interface. Nat Commun. 2017;8(1):1-9.
14. Choudhury S, Stalin S, Vu D, et al. Solid-state polymer electrolytes for high-performance lithium metal batteries. Nat Commun. 2019;10(1):1-8.
15. Yu S, Schmohl S, Liu Z, et al. Insights into a layered hybrid solid electrolyte and its application in long lifespan high-voltage all-solid-state lithium batteries. J Mater Chem A. 2019;7 (8):3882-3894.
16. Jiang Z, Han Q, Wang S, Wang H. Reducing the interfacial resistance in all-solid-state lithium batteries based on oxide ceramic electrolytes. ChemElectroChem. 2019;6(12):2970-2983.
17. Leng F, Tan CM, Pecht M. Effect of temperature on the aging rate of Li ion battery operating above room temperature. Sci Rep. 2015;5:1-12.
18. Ma S, Jiang M, Tao P, et al. Temperature effect and thermal impact in lithium-ion batteries: a review. Prog Nat Sci Mater Int. 2018;28(6):653-666.
19. Cheng M, Ramasubramanian A, Rasul MG, et al. Direct ink writing of polymer composite electrolytes with enhanced thermal conductivity. Adv Funct Mater. 2020;31:2006683.
20. Wang C, Sun Q, Liu Y, et al. Boosting the performance of lithium batteries with solid-liquid hybrid electrolytes: interfacial properties and effects of liquid electrolytes. Nano Energy. 2018;48(March):35-43.
21. Liang JY, Zhang XD, Zeng XX, et al. Enabling a durable electrochemical Interface via an artificial amorphous cathode electrolyte interfacephase for hybrid solid/liquid lithium-metal batteries. Angew Chem - Int Ed. 2020;59(16):6585-6589.
22. Xu L, Tang S, Cheng Y, et al. Interfaces in solid-state lithium batteries. Joule. 2018;2(10):1991-2015.
23. Luo W, Gong Y, Zhu Y, et al. Reducing interfacial resistance between garnet-structured solid-state electrolyte and Li-metal anode by a germanium layer. Adv Mater. 2017;29(22):1-17.
24. Chen H, Liu QY, Jing MX, et al. Improved interface stability and room-temperature performance of solid-state lithium batteries by integrating cathode/electrolyte and graphite coating. ACS Appl Mater Interfaces. 2020;12(13):15120-15127.
25. Gutiérrez-Pardo A, Pitillas Martínez AI, Otaegui L, et al. Will the competitive future of solid state Li metal batteries rely on a ceramic or a composite electrolyte? Sustain Energy Fuels. 2018;2(10):2325-2334.
26. Liu Q, Zhou D, Shanmukaraj D, et al. Self-healing Janus interfaces for high-performance LAGB-based lithium metal batteries. ACS Energy Lett. 2020;5(5):1456-1464.
27. Pitillas Martínez AI, Aguesse F, Otaegui L, et al. The cathode composition, a key player in the success of Li-metal solid-state batteries. J Phys Chem C. 2019;123(6):3270-3278.
28. Li Y, Zhou W, Chen X, et al. Mastering the interface for advanced all-solid-state lithium rechargeable batteries. Proc Natl Acad Sci. 2016;113(47):13313-13317.
29. Park M, Shin DS, Ryu J, et al. Organic-catholyte-containing flexible rechargeable lithium batteries. Adv Mater. 2015;27(35):5141-5146.
30. Zhao Y, Guo J. Development of flexible Li-ion batteries for flexible electronics. InfoMat. 2020;2(5):866-878.
31. Porcarelli L, Gerbaldi C, Bella F, Nair JR. Super soft all-ethylene oxide polymer electrolyte for safe all-solid lithium batteries. Sci Rep. 2016;6(1):16892.
32. Xia S, Wu X, Zhang Z, Cui Y, Liu W. Practical challenges and future perspectives of all-solid-state lithium-metal batteries. Chem. 2019;5(4):753-785.
33. de Klerk NJJ. Simulations of electrode & solid electrolyte materials. TU Delft Univ. 2019;1-177.
34. Oh P, Lee H, Park S, Cha H, Kim J, Cho J. Improvements to the overpotential of all-solid-state lithium-ion batteries during the past ten years. Adv Energy Mater. 2020;10:2000904.
35. Devaux D, Leduc H, Dumaz P, Lecuyer M, Deschamps M, Bouchet R. Effect of electrode and electrolyte thicknesses on all-solid-state battery performance analyzed with the sand equation. Front Energy Res. 2020;7(January):1-10.
36. Lai W, Haile SM. Impedance spectroscopy as a tool for chemical and electrochemical analysis of mixed conductors: A case study of ceria. J Am Ceram Soc. 2005;88:2979-2997.
37. Chen X, Vereecken PM. Solid and solid-like composite electrolyte for lithium ion batteries: engineering the ion conductivity at interfaces. Adv Mater Interfaces. 2019;6(1):1-31.
38. Westerhoff U, Kurbach K, Lienesch F, Kurrat M. Analysis of lithium-ion battery models based on electrochemical impedance spectroscopy. Energy Technol. 2016;4(12):1620-1630.
39. Rodrigues S, Munichandraiah N, Shukla AK. AC impedance and state-of-charge analysis of a sealed lithium-ion rechargeable battery. J Solid State Electrochem. 1999;3(7-8):397-405.
40. Yu X, Manthiram A. Electrode-electrolyte interfaces in lithium-based batteries. Energy Environ Sci. 2018;11(3):527-543.
41. Nara H, Morita K, Mukoyama D, Yokushima T, Momma T, Osaka T. Impedance analysis of LiNi1/3Mn1/3Co1/3 cathodes with different secondary-particle size distribution in Lithium-ion battery. Electrochim Acta. 2017;241:323-330.
42. Huang J. Diffusion impedance of electroactive materials, electrolytic solutions and porous electrodes: Warburg impedance and beyond. Electrochim Acta. 2018;281:170-188.
43. Song J, Bazant MZ. Effects of nanoparticle geometry and size distribution on diffusion impedance of battery electrodes. J Electrochem Soc. 2013;160(1):A15-A24.
44. Wang C, Appleby AJ, Little FE. Electrochemical impedance study of initial lithium ion intercalation into graphite powders. Electrochim Acta. 2001;46(12):1793-1813.
45. Scipioni R, Jorgensen PS, Ngo D-T, et al. Low-voltage FIB/SEM tomography for 3D microstructure evolution of LiFePO4/C electrode. ECS Trans. 2015;69(18):71-80.
46. Ding Z, Li J, Li J, An C. Interfaces: key issue to be solved for all solid-state lithium battery technologies. J Electrochem Soc. 2020;167(7):070541.
47. Rojaee R, Cavallo S, Mogurampelly S, et al. Highly-cyclable room-temperature phosphorene polymer electrolyte composites for Li metal batteries. Adv Funct Mater. 2020;30:1910749.
48. Yuan H, Luan J, Yang Z, et al. Single lithium-ion conducting solid polymer electrolyte with superior electrochemical stability and interfacial compatibility for solid-state lithium metal batteries. ACS Appl Mater Interfaces. 2020;12(6):7249-7256.
49. Ding Z, Li J, Li J, An C. Review—interfaces: key issue to be solved for all solid-state lithium battery technologies. J Electrochem Soc. 2020;167(7):070541.
50. Kaneko F, Wada S, Nakayama M, Wakahara M, Koki J, Kuroki S. Capacity fading mechanism in all solid-state lithium polymer secondary batteries using PEG-borate/alkalinate ester as plasticizer for polymer electrolytes. Adv Funct Mater. 2009;19(6):918-925.
51. Logan ER, Dahn JR. Electrolyte design for fast-charging Li-ion batteries. Trends Chem. 2020;2(4):354-366.
52. da Rosa CG, Sganzerla WG, de Oliveira Brisola Maciel MV, et al. Development of poly (ethylene oxide) bioactive nanocomposite films functionalized with zein nanoparticles. Colloids Surf A Physicochem Eng Asp. 2020;586:124268.
53. Rasul MG, Kiziltas A, Malliakas CD, et al. Polyethylene-BN nanosheets nanocomposites with enhanced thermal and mechanical properties. Compos Sci Technol. 2021;204:108631.
54. Kim GT, Appetecchi GB, Carewska M, et al. UV cross-linked, lithium-conducting ternary polymer electrolytes containing ionic liquids. J Power Sources. 2010;195(18):6103-6137.
55. An SJ, Li J, Du Z, Daniel C, Wood DL. Fast formation cycling for lithium ion batteries. J Power Sources. 2017;342:846-852.
56. Evans J, Vincent CA, Bruce PG. Electrochemical measurement of transference numbers in polymer electrolytes. Polymer (Guildf). 1987;28(13):2324-2328.
57. Ziemann S, Fleischmann M, Amereller M, Gschwind RM, Wiemhöfer HD, Gores HJ. Measurement of transference...
numbers for lithium ion electrolytes via four different methods, a comparative study. *Electrochim Acta*. 2011;56(11): 3926-3933.

**SUPPORTING INFORMATION**

Additional supporting information may be found online in the Supporting Information section at the end of this article.

**How to cite this article:** Rojaee R, Plunkett S, Rasul MG, Cheng M, Jabbari V, Shahbazian-Yassar R. Interfacial engineering of lithium-polymer batteries with in situ UV cross-linking. *InfoMat*. 2021;1–12. [https://doi.org/10.1002/inf2.12197](https://doi.org/10.1002/inf2.12197)