All-Solid-State Lithium Batteries: Li⁺-Conducting Ionomer Binder for Dry-Processed Composite Cathodes

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ABSTRACT: All-solid-state lithium batteries (ASSLBs) are considered promising alternatives to current lithium-ion batteries as their use poses less of a safety risk. However, the fabrication of composite cathodes by the conventional slurry (wet) process presents technical challenges, such as limited stability of sulfide electrolytes against organic solvents and the increase of ionic resistance due to the use of insulating polymer binder. Herein, we develop a composite cathode fabricated using a solvent-free (dry) process. The composite cathode is prepared with a Li⁺-conducting ionomer binder, poly(tetrafluoroethylene-co-perfluoro(3-oxa-4-pentenesulfonic acid)) lithium salt. The ionomer facilitates Li⁺ transport and ensures good interfacial contact between the active material (LiNi₀.7Co₀.1Mn₀.2O₂), conducting carbon, and solid electrolyte (Li₆PS₅Cl) during cycling. Consequently, an ASSLB featuring a composite cathode with an ionomer delivers a high discharge capacity of 180.7 mAh g⁻¹ (3.05 mAh cm⁻²) at 0.1 C and demonstrates stable cycling performance, retaining 90% of its initial capacity after 300 cycles at 0.5 C.

Global warming and the resulting environmental regulations are driving the development of environmentally friendly transportation systems,¹⁻³ for example, electric vehicles (EVs) employing lithium-ion batteries (LIBs). However, the use of LIBs poses a significant safety risk as they typically contain a highly flammable liquid electrolyte, which can lead to a fire or an explosion under abnormal operating conditions.⁴⁻⁷ Accordingly, all-solid-state lithium batteries (ASSLBs) employing solid electrolytes are considered promising alternatives to current LIBs.⁸⁻¹¹ Various solid electrolytes (polymer, inorganic, and composite electrolytes) that demonstrate high ionic conductivity and exhibit good interfacial contact with electrodes have been developed to improve the cycling performance of ASSLBs.¹²⁻¹⁵ Among them, sulfide-based solid electrolytes, such as Li₁₀GeP₂S₁₂, Li₄PS₅X (X = Cl, Br, I) argyrodites, and Li₄S–P₂S₆, exhibit the highest ionic conductivities (on the order of 10⁻² S cm⁻¹) at room temperature, comparable with those of liquid electrolytes.¹⁶⁻¹⁹ Moreover, their ductility facilitates the large-scale production of cells, since it eliminates the need for sintering at high temperature, improving the processability of electrolytes and electrodes for ASSLBs. Nevertheless, the realization of sulfide-based ASSLBs is challenging due to the difficulty of
producing sheet-type electrodes with high active mass loading. To avoid the delamination of cathode components (active material, conducting carbon, and solid electrolyte) and mitigate mechanical stress generated during cycling, a small amount of polymer binder is usually incorporated into the composite cathode. A slurry (wet) process is typically used to fabricate composite cathodes, such as those used in LIBs. However, slurry processes present several technical challenges, such as the reactivity of sulfide electrolytes with organic solvents and the increase of ionic resistance due to the presence of insulating polymer binder like nitrile butadiene rubber (NBR), resulting in the degradation of cell performance. To overcome the challenges of slurry processes, solvent-free (dry) processing has been considered. A representative polymer binder for the dry process is polytetrafluoroethylene (PTFE), which forms fibrous linear binding and enables the manufacture of sheet-type composite cathodes. PTFE is known to be electrochemically stable at high voltage and does not react with cathode active materials. However, the ability of PTFE to conduct lithium ions is limited, and it is unable to ensure sufficient interfacial adhesion between the active material, solid electrolyte, and conducting carbon. Therefore, we explore a Li+-conducting ionomer as a binder in the solvent-free dry process of a composite cathode for ASSLB. Particularly, poly(tetrafluoroethylene-co-perfluoro-(3-oxa-4-pentenesulfonic acid)) lithium salt (denoted as ionomer hereafter) demonstrates high ionic conductivity and good adhesive properties. As a result, a composite cathode prepared with the ionomer enables the realization of an ASSLB featuring a composite cathode prepared with PTFE.

The FT-IR spectra of PTFE and the PTFE-based ionomer are shown along with their chemical structures in Figure S1a,b, respectively. In addition to peaks attributable to PTFE, the FT-IR spectrum of the PTFE-based ionomer shows new peaks at 970 and 1060 cm⁻¹, corresponding to C−O−C and SO₄²⁻ groups, respectively. The molar ratio of tetrafluoroethylene to perfluoro(3-oxa-4-pentenesulfonic acid) lithium salt in the ionomer (with an equivalent weight of 790 g mol⁻¹ SO₄Li) was determined to be 5:1 by X-ray fluorescence spectrometry. The ionic conductivities of Li₆PS₅Cl, Li₆PS₅Cl−PTFE, and Li₆PS₅Cl−ionomer composites (with the same composition as that of the corresponding composite cathodes, i.e., Li₆PS₅Cl−binder = 25:2 by weight) were determined by AC impedance spectroscopy (Figure S2). The ionic conductivity of Li₆PS₅Cl, 4.1 mS cm⁻¹, exceeds that of the Li₆PS₅Cl−PTFE composite, 2.9 mS cm⁻¹ (Figure S1c), because PTFE is a nonconductive polymer. It should be noted that the ionic conductivity of the Li₆PS₅Cl−ionomer composite is higher than that of the Li₆PS₅Cl−PTFE composite, indicating that the ionomer is a better conductor of Li⁺ ions than PTFE. The ionic conductivity of the ionomer in the fully dry state was measured to be 1.6 × 10⁻⁸ S cm⁻¹ at 25 °C. The contribution of the ionomer to the ionic conductivity of the Li₆PS₅Cl−ionomer composite was investigated by Li solid-state magic-angle spinning (MAS) NMR spectroscopy. The Li solid-state MAS NMR spectra of the Li₆PS₅Cl−ionomer composite were analyzed before and after its subjection to galvanostatic stripping/deposition cycles in a symmetric Li/Li₆PS₅Cl−ionomer composite/Li cell at a current density of 0.1 mA cm⁻² for 2 h. Figure S1d shows the Li solid-state MAS NMR spectra of the Li₆PS₅Cl−ionomer composite before and after cycling. The spectra can be resolved into two peaks that are centered at 2.5 and −0.2 ppm, corresponding to characteristic Li peaks of Li₆PS₅Cl and the ionomer, respectively, as shown in Figure S3a,b. The intensities of the Li peaks (corresponding to both Li₆PS₅Cl and the ionomer) in the spectrum of the Li₆PS₅Cl−ionomer composite after cycling are lower than those of the Li peaks in the spectrum obtained prior to cycling. This is because some Li⁺ ions in Li₆PS₅Cl and the ionomer are replaced with Li⁺ ions during cycling in the Li/Li₆PS₅Cl−ionomer composite/Li cell, as illustrated in Figure S3c. These results demonstrate that Li⁺ ions are conducted by the ionomer as well as Li₆PS₅Cl, which is consistent with the ionic conductivity results. It should be noted that the large amount of Li still remains in the Li₆PS₅Cl−ionomer composite after cycling. It can be ascribed to low areal capacity (0.2 mA h cm⁻²) and high areal mass of the Li₆PS₅Cl−ionomer composite (122 mg cm⁻²) in the galvanostatic cycling. Long-term electrochemical impedance spectroscopy of the Li₆PS₅Cl−ionomer composite was performed at 55 °C to verify the compatibility between them. We prepared the composite with Li₆PS₅Cl and ionomer at a mass ratio of 25:2, which is the same as the ratio of the composite cathode. As can be seen in Figure S4, the bulk resistance of the composite is not changed with time at elevated temperature. This result indicates that the ionomer is highly compatible with sulfide electrolyte (Li₆PS₅Cl) without side reactions. The cyclic voltammograms of the Li₆PS₅Cl−binder composites (Figure S5) confirm that both PTFE and the ionomer are electrochemically stable up to 3.9 V vs Li−In (4.5 V vs Li/Li⁺).

Composite cathodes were prepared by mixing an active material (LiNi₀.7Co₀.1Mn₀.2O₂; NCM), a solid electrolyte (Li₆PS₅Cl), conducting carbon (carbon nanofiber), and a polymer binder (PTFE or ionomer) at a mass ratio of 70:25:3:2. NCM particles with different particle sizes (4 and 10 μm, Figure S6) were used to maximize the contact area between the NCM particles and solid electrolyte through optimal packing. When XRD patterns of the composite cathode are analyzed over time (Figure S7), it is confirmed that NCM has good chemical stability toward Li₆PS₅Cl without any degradation in the composite cathode. A cross-sectional SEM image of a composite cathode prepared with the ionomer (Figure S8a) shows good interfacial contact between the NCM particles, solid electrolyte, and conducting carbon. Its energy-dispersive X-ray spectroscopy (EDS) reveals the uniform distribution of the fluorine atoms in the PTFE-based ionomer throughout the composite cathode. A cross-sectional SEM image of a composite cathode prepared with PTFE (Figure S8b) shows the presence of fibers, which is consistent with the observations of a previous study that used PTFE when making the composite cathode. These fiber-like binding structures of PTFE form as a result of its high crystallinity.

In contrast, the ionomer is evenly distributed and does not form fiber-like structures, resulting in strong adhesion and good interfacial contact between the components of the composite cathode. A TOF-SIMS image mapping the SO₄²⁻ groups of a composite cathode prepared with the ionomer (Figure S9) confirms its homogeneous distribution. The uniformly dispersed ionomer provides continuous pathways for the conduction of Li⁺ ions and enhances the interfacial contact between the components of the composite cathode.

The cycling performance of cells featuring composite cathodes prepared without a binder, with PTFE, and with the ionomer was investigated at 0.5 C. The mass loading of
NCM in the composite cathodes was 16.9 mg cm$^{-2}$. Each cell was first subjected to successive conditioning cycles at 0.05 C (twice) and 0.1 C (once); the voltage profiles for the first cycle at 0.05 C and the third cycle at 0.1 C are shown in Figures S10a and 1a, respectively. The composite cathode prepared with ionomer delivers the highest discharge capacity at 0.1 C, i.e., 180.7 mAh g$^{-1}$ based on active NCM material, corresponding to an areal capacity of 3.05 mAh cm$^{-2}$. The voltage profiles of the cells at 0.5 C are presented in Figure S10b–d, and the cycling performances of the cells are compared in Figure 1b. The cell featuring a cathode without binder suffers severe capacity loss during cycling while the cell featuring a composite cathode prepared with PTFE demonstrates fair capacity retention up to the 150th cycle, before suffering large capacity fading. The delayed capacity loss is ascribed to the limitation of adhesion strength through fibrous binding during the repeated expansion and contraction of the active NCM materials.35 As the volume changes repeatedly during cycling, the critical point for maintaining the strong binding was reached; thus, the interparticle contacts in the composite cathodes would be loose above the limit. In contrast, the cell employing a composite cathode prepared with the ionomer exhibits excellent cycling stability with Coulombic efficiency higher than 99.5% on average through cycling, retaining 90% of its initial discharge capacity after 300 cycles. When comparing cycling performance of sulﬁde-based ASSLBs reported to date, the cell with composite cathode employing the ionomer binder in this work exhibited the best cycling stability even at the highest areal capacity (Table S1). Figure 1c,d shows the AC impedance spectra of cells featuring composite cathodes prepared without a binder, with PTFE, and with the ionomer after the 1st and 300th cycles, respectively. The $x$-axis intercept corresponds to the bulk resistance of the solid electrolyte, while the depressed semicircle in the high- to mid-frequency range is attributed to interfacial resistance at the electrode–electrolyte interface, including charge-transfer resistance between NCM and LiPS$_5$Cl.36,37 The $x$-axis intercepts of the AC impedance spectra of the cells are almost the same, indicating that the bulk resistance of the solid electrolyte is not affected by the binder.

Figure 1. (a) Voltage profiles of the conditioning cycles of ASSLBs featuring different composite cathodes at 0.1 C. (b) Cycling performance of ASSLBs, cycled at 0.5 C and 25 °C. AC impedance spectra of ASSLBs after the (c) 1st and (d) 300th cycles at 25 °C. (e) Discharge curves of an ASSLB featuring a composite cathode prepared with the ionomer. (f) Rate capabilities of ASSLBs featuring different composite cathodes at 25 °C.
However, the cell featuring a composite cathode prepared with the ionomer not only exhibits the lowest interfacial resistance but also experiences the lowest increase in the interfacial resistance after 300 cycles. These results suggest that the ionomer binder maintains good interfacial contact between NCM, Li6PS5Cl, and the conducting carbon during the repeated cycling. The rate capabilities of the cells were evaluated at different current densities. As depicted in Figure 1e, the cell featuring a composite cathode prepared with the ionomer exhibits a low overpotential even at a high current density, resulting in a high discharge capacity at a high C rate (123.4 mAh g\(^{-1}\) at 2.0 C). In contrast, the cell employing a composite cathode prepared without binder delivers the lowest discharge capacities at all the C rates investigated (Figure 1f). These results are well consistent with the AC impedance results, revealing that the binder-free cell has the highest cell resistance.

The direct current internal resistance (DC-IR) of cells featuring composite cathodes with different binders was determined experimentally. During each experiment, the cell was first charged and discharged at 0.05 C, then charged to 3.1 V and rested for 1 h, and finally, at increasing C rates, charged for 10 s, rested for 20 min, discharged for 10 s, and rested for 20 min. The voltage responses of the cells are shown in Figure 2a,b. The internal resistance of each cell during charge and discharge is determined by the linear regression analysis of plots of the change in voltage vs current (ΔV−i) (Figure 2c,d). In both cells, the slopes for the discharge process exceed those for the charge process; this is because the intercalation of Li\(^+\) into NCM is slower than the deintercalation of Li\(^+\) from NCM.\(^{39}\) The slopes of the ΔV−i plots in the cell employing ionomer are comparatively low, indicating that the ionomer is better than PTFE for reducing the internal resistance of the ASSLB, since it conducts Li\(^+\) ions unlike PTFE. The galvanostatic intermittent titration technique (GITT) was used to assess the role of the binder in the composite cathodes.\(^{23,40}\) The obtained voltage profiles and polarization curves of cells assembled with different composite cathodes are shown in Figure 2e. The cell employing a composite cathode with ionomer exhibits the lowest polarization; this is due to the ability of the ionomer to conduct Li\(^+\) ions and enhance the interfacial contact between the...
components in the composite cathode. The relative active surface area of the NCM in the composite cathodes can be calculated from the GITT results (Figure S11).41 When one takes the active surface area of the NCM in the composite cathode prepared without binder as 1.0 S, the relative active surface areas of the NCM in the composite cathodes prepared with PTFE and with the ionomer are 1.52 and 2.17 S, respectively (Figure 2f). These results suggest that the ionomer enables strong adhesion between the NCM particles and solid electrolyte through its uniform dispersion in the composite cathode, facilitating the interfacial transport of Li$^+$ ions through the enhanced active surface area.

Cross-sectional morphologies of composite cathodes were examined by SEM images before and after 300 cycles to investigate the effect of binder on the interfacial contact after long-term cycling (Figure 3).

Before cycling, the pristine composite cathodes prepared without binder, with PTFE, and with the ionomer showed good adhesion between their components in the electrodes, indicating that good interfacial contact between electrode components can be achieved by cold pressing owing to the ductility of Li$_6$PS$_5$Cl. The slightly reduced porosity in the composite cathode with the ionomer arises from efficient pore filling with polymer binder during pressing at 430 Ma due to the elastic property of the ionomer. After long-term cycling (300 cycles), the composite cathodes prepared without binder and with PTFE showed large voids between NCM particles and the solid electrolyte; this loss of interfacial contact between the NCM particles and solid electrolyte results from the mechanical stress caused by the large volumetric changes of NCM during charge and discharge cycling.42−44 The loss of the electrical conduction pathway due to the presence of large voids in these electrodes is likely the main cause of large capacity fading during cycling (Figure 1b). In contrast, the interfacial contact between active NMC materials and solid electrolyte in the composite cathode prepared with the ionomer was well maintained after long-term cycling; i.e., the incidence of voids in the cycled composite cathode was low, which resulted in good cycling stability.

To investigate the adhesive strength between the components in the composite cathodes, surface and interfacial cutting analysis system (SAICAS) experiments were performed,45,46 as schematically illustrated in Figure 4a,b. Both the horizontal and vertical forces were measured during the cutting and peeling processes of the experiment. As shown in Figure 4c,d, the horizontal and vertical forces required to cut and peel the composite cathode prepared with the ionomer are much higher than those required for the composite cathode prepared with PTFE, indicating the superior adhesive strength of the ionomer. A nanoindentation experiment was also performed to compare the elastic recovery of the composite cathodes prepared with PTFE and the ionomer. On the basis of the nanoindentation curves of the composite cathodes prepared with PTFE and with the ionomer (Figure S12), their elastic recovery ratios (i.e., their restored depths divided by their penetrated depths) are 0.47 and 0.66, respectively.47,48 The higher elastic recovery ratio of the composite cathode prepared with the ionomer indicates that it can withstand mechanical stress due to the volumetric changes of the active material during charging and discharging, accounting for the good cycling stability of the corresponding cell.

After obtaining the results of our investigations, we illustrated the morphologies of the composite cathodes prepared with PTFE and with the ionomer in Figure 5.

Figure 3. Cross-sectional SEM images of pristine composite cathodes prepared (a) without binder, (b) with PTFE, and (c) with the ionomer. Cross-sectional SEM images of cycled composite cathodes prepared (d, g) without binder, (e, h) with PTFE, and (f, i) with the ionomer (after 300 cycles).
Although PTFE can be used as a binder in the dry-processed composite cathode, it is unable to maintain strong adhesion between the components of composite cathodes with high mass loadings during long-term cycling (Figure 5a). Moreover, PTFE hinders the transport of Li$^+$ in the composite cathode because it is an insulating polymer. These limitations can be eliminated by using a Li$^+$-conducting ionomer with good adhesive properties as the binder. Unlike PTFE, the ionomer disperses uniformly throughout the composite cathode, enabling it to maintain good interfacial contact between the active material and solid electrolyte during cycling. Moreover, the presence of a Li$^+$-conducting ionomer at the active NCM material—solid electrolyte interface facilitates Li$^+$ transport (Figure 5b). Consequently, the ASSLB employing a composite cathode prepared with the ionomer demonstrates excellent cycling stability and high rate capability.

Figure 4. (a) Schematic illustration of a SAICAS experiment. (b) Photographs showing the cutting/peeling of a composite cathode using a cutting blade. (c) Horizontal and (d) vertical forces required to cut and peel the composite cathodes prepared with PTFE and with the ionomer.

The commercialization of sulfide-based ASSLBs has been hindered by performance limitations associated with the processes used to fabricate composite cathodes. In particular, organic solvents used in typical slurry (wet) processes cause structural damage to solid sulfide electrolytes while insulating polymer binders increase ionic resistance in the composite cathode. In this study, a PTFE-based ionomer with high Li$^+$ conductivity and good adhesive properties was proposed as a binder for the solvent-free (dry) processing of composite cathodes. Unlike insulating PTFE, the most prevalently employed binder for the dry processing of composite cathodes, the ionomer facilitates Li$^+$ transport and ensures good interfacial contact owing to its uniform distribution throughout the composite cathode. As a result, the cycling performance of a cell featuring a composite cathode prepared with the ionomer was superior to that of a cell featuring a composite cathode...
prepared with PTFE in terms of discharge capacity (180.7 mAh g\(^{-1}\) vs 176.7 mAh g\(^{-1}\) at 0.1 C), cycling stability (90% vs 24% capacity retention after 300 cycles at 0.5 C), and rate capability (123.4 mAh g\(^{-1}\) vs 76.2 mAh g\(^{-1}\) at 2.0 C). Evidently, the proposed ionomer is a promising polymer binder for the solvent-free processing of composite electrodes for high-performance ASSLBs with good cycling stability and high rate capability.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.1c02756.

Methods, FT-IR spectra of PTFE and the ionomer, ionic conductivities of Li\(_6\)PS\(_5\)Cl and the composites, \(^7\)Li solid-state MAS NMR spectra of the Li\(_6\)PS\(_5\)Cl–ionomer composite, AC impedance spectra of Li\(_6\)PS\(_5\)Cl and the composites, \(^7\)Li solid-state MAS NMR spectra of the Li\(_6\)PS\(_5\)Cl–ionomer composite before and after cycling and a schematic of the substitution of \(^7\)Li with \(^6\)Li, AC impedance spectra of the Li\(_6\)PS\(_5\)Cl–ionomer composite at 55 °C, cyclic voltammograms of the composite cathode, cross-sectional SEM images of the composite cathodes, TOF-SIMS image of a composite cathode prepared with the ionomer, voltage profiles of the first conditioning cycles of the all-solid-state cells, charge and discharge curves of cells with different composite cathodes at 0.5 C, cycling performance of sulfide-based ASSLBs, potential responses of cells during two GITT pulses, and nanoindentation curves of the composite cathodes (PDF)

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**Notes**

The authors declare no competing financial interest.
This work was supported by LG Energy Solution, the National Research Foundation of Korea funded by the Korean government (2021R1A2C2011050), and the Technology Innovation Program (2001230) funded by the Ministry of Trade, Industry and Energy (MOTIE, Korea).

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