



Digital-twin-driven structural and electrochemical analysis of Li⁺ single-ion conducting polymer electrolyte for all-solid-state batteries

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Funding information

Ministry of Science and ICT, South Korea, Grant/Award Number: NRF-2022M3J1A1054326; Ministry of Trade, Industry and Energy, Grant/Award Number: 20012326

Abstract

The electrode structure is a crucial factor for all-solid-state batteries (ASSBs) since it affects the electronic and ionic transport properties and determines the electrochemical performance. In terms of electrode structure design, a single-ion conducting solid polymer electrolyte (SIC-SPE) is an attractive solid electrolyte (SE) for the composite electrode among various SEs. Although the ionic conductivity of SIC-SPE is lower than other inorganic SEs, the SIC-SPE has a relatively lower density and can form an intimate contact between the SE and active materials (AM), resulting in an excellent electrode structure. The electrochemical performance of the cell with SIC-SPE was comparable with the cell with Li6PS5Cl (LPSCl), which has 10 times higher intrinsic ionic conductivity than SIC-SPE (SIC-SPE: $0.2 \times 10^{-3} \text{ S cm}^{-1}$, LPSCl: $2.2 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C). 3D digital-twin-driven simulation showed that the electrode with SIC-SPE has a higher SE volume fraction, a lower tortuosity, and a larger AM/SE contact area than the LPSCl electrode. The favorable structure of the SIC-SPE electrode leads to lower overpotential than the LPSCl electrode during operation. Our results suggest that the SIC-SPE is a promising SE for making a good electrode structure in ASSBs.

KEYWORDS

all-solid-state batteries, digital-twin simulation, electrode design, single ion conducting solid polymer electrolyte

1 | INTRODUCTION

The increased demand for improved safety of lithium secondary batteries for electric vehicles has resulted in research on all-solid-state batteries (ASSBs) being

actively conducted.^{1–3} The low flammability of solid electrolytes (SEs) provides resistance to fire and explosion incidents. Additionally, high energy density can be achieved by using high-voltage cathode materials owing to the wider electrochemical window of SEs.^{4,5} Previous

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studies on SEs for ASSBs have mainly focused on inorganic SEs, such as sulfides and oxides. Inorganic SEs have a remarkable property of high ionic conductivity (10^{-2} – 10^{-4} S cm $^{-1}$ at 25°C) with a lithium transference number (t_{Li^+}) close to unity. Moreover, the mechanical rigidity of inorganic SEs suppresses the growth of Li dendrites. However, several problems with using inorganic SEs in ASSBs must be solved. In the electrode, high pressure or sintering process is required to ensure contact between active material (AM)/SE or SE/SE.^{6,7} Even after these additional processes, spaces inevitably remain between electrode materials.^{6–8} High thickness and interfacial/grain boundary resistance in the electrolyte are other problems associated with inorganic SEs.^{1,9,10}

As regards the above-mentioned issues of inorganic SEs, solid polymer electrolytes (SPEs) are being revisited as promising electrolytes for ASSBs.^{11–13} This is because SPEs can form intimate contact with the AM of electrodes, ensuring a large AM-SE interfacial area.^{13,14} Moreover, in contrast to inorganic SEs, which require high external pressures during manufacturing and operation to form and maintain interfacial contacts, SPEs do not require high-pressure levels. This not only simplifies the manufacturing process but also improves energy density. Furthermore, due to their good processability and formability, SPEs are suitable for large-area cell design and mass production (Figure 1).

Notwithstanding these advantages, a major impediment to the practical application of SPEs is low ionic conductivity ($<10^{-4}$ S cm $^{-1}$ at 25°C). Furthermore, many of the reported studies on SPEs have focused on dual-ion conductors composed of Li salts and polymers with low t_{Li^+} (<0.5). Since only Li $^+$ can electrochemically react within both electrodes, the low t_{Li^+} implied that less than 50% of the total ionic conductivity actually contributes to the battery performance. Moreover, a low t_{Li^+} causes local ion polarization during cycling and leads to uneven Li $^+$ deposition, thus resulting in Li dendrite formation and power density degradation.^{12,15}

In this study, to address the low t_{Li^+} of dual-ion conducting SPEs, we present a sulfonated tetrafluoroethylene copolymer-based single-ion conducting SPE (SIC-SPE) with an ionic conductivity of 0.2×10^{-3} S cm $^{-1}$ at 25°C for application in ASSBs. The high ionic conductivity of SIC-SPE with a t_{Li^+} close to unity provides reliable electrochemical performance and rate capability for ASSBs. Furthermore, a virtual 3D electrode structure obtained by 3D digital-twin simulation demonstrated that the electrodes with SIC-SPE have a larger AM/SE interface and a well-connected percolation pathway than those with inorganic SEs. These structural advantages led to a lower overpotential in the electrodes.¹⁶ This study highlights the prospect of SIC-SPEs, and future research directions and developments for practical applications are discussed.

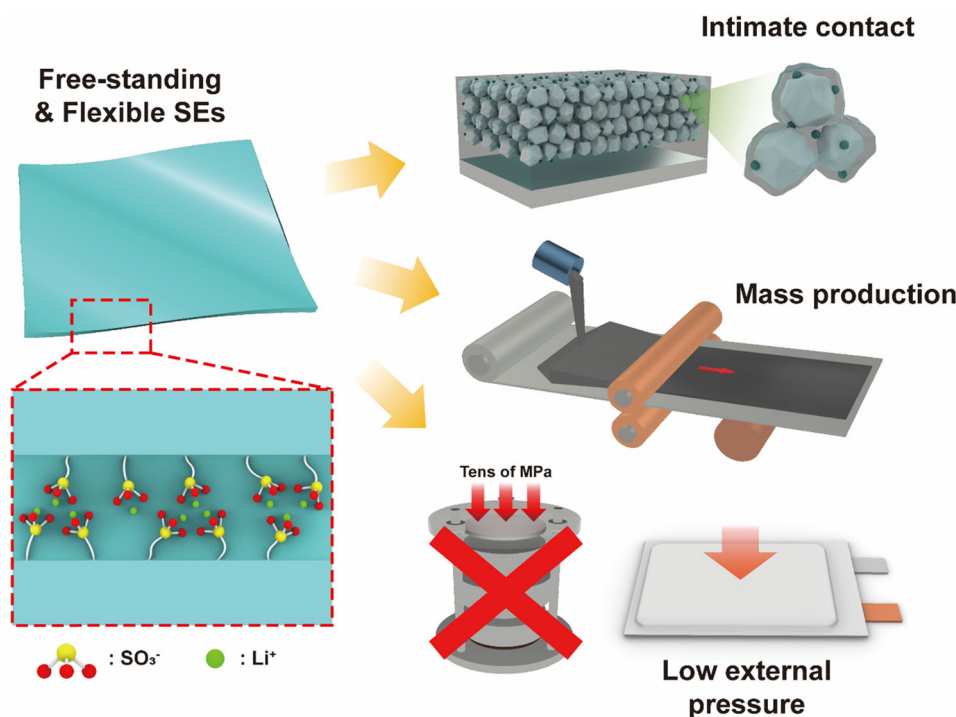


FIGURE 1 A schematic of promising advantages of single-ion conducting solid polymer electrolyte (SIC-SPE) for ASSB applications. ASSB, all-solid-state batteries; SE, solid electrolytes.

2 | RESULTS AND DISCUSSION

The SIC-SPE, Li⁺-substituted sulfonated tetrafluoroethylene copolymer (Supporting Information: Figure S1), could be fabricated into a freestanding film of 30 μm thickness, which is the target level of

rigid inorganic solid electrolytes. Moreover, the SIC-SPE film was flexible enough to withstand mechanical deformations, such as twisting and folding (Supporting Information: Figure S2). Furthermore, the ionic conductivity (σ) of the SIC-SPE, $0.2 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C and $6.1 \times 10^{-3} \text{ S cm}^{-1}$ at 60°C (Figure 2A), is not

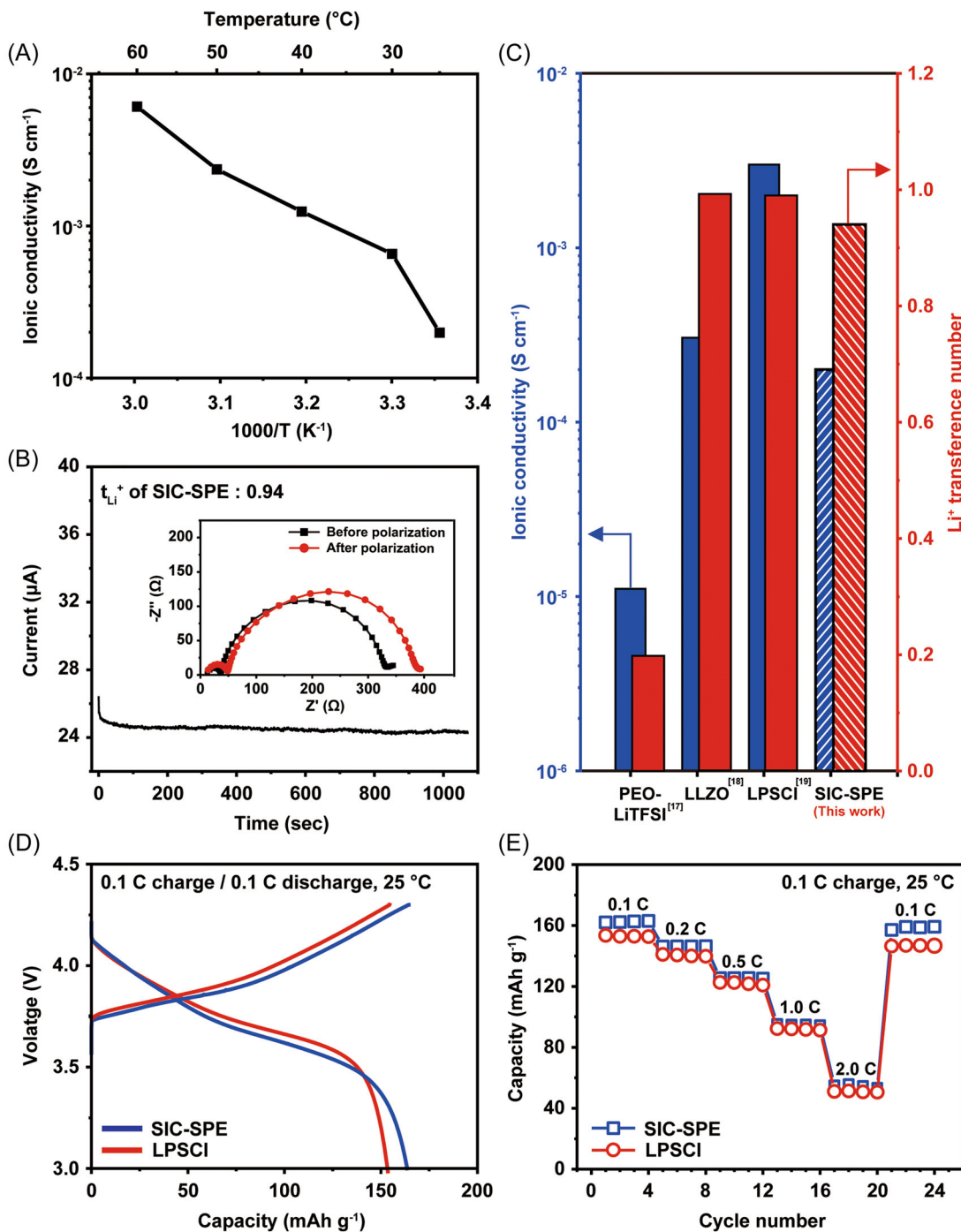


FIGURE 2 (A) Ionic conductivity values of the SIC-SPE as a function of temperature (B) Li⁺ transference number measurement profile of SIC-SPE based on chronoamperometry and EIS. (C) Comparative bar chart of ion conductivities and Li⁺ transference numbers of SIC-SPE and other SEs.^{17–19} (D) Charge/discharge voltage profiles of SIC-SPE and LPSCI (Li₆PS₅Cl)-based ASSBs at 0.1 C. (E) Rate capability of each ASSB cell from 0.1 to 2 C. ASSB, all-solid-state batteries; EIS, electrochemical impedance spectroscopy, SEs, solid electrolytes; SIC-SPE, single-ion conducting solid polymer electrolyte.

only higher than those of many other reported SPEs but also comparable with other ion-conductive inorganic solid electrolytes (Supporting Information: Table S1). The SIC-SPE can be utilized for room temperature operation owing to a σ of $>10^{-4} \text{ S cm}^{-1}$ at 25°C. The lithium transference number (t_{Li^+}) of the SIC-SPE was 0.94, indicating that it is a single-ion conductor, similar to other inorganic solid electrolytes (Figure 2B,C).^{17–19} The lithium plating/stripping characteristics of SIC-SPE were evaluated using Li/SIC-SPE/Cu and Li/SPE/Li cells and showed that SIC-SPE could be utilized as SE for an ASSB system as shown in Supporting Information: Figures S3 and S4.

To evaluate the flame-retardancy of the SIC-SPE, its film was exposed to flame as shown in Supporting Information: Figure S5, with the original shape being well maintained after the test. Additionally, the electrochemical stability of the SIC-SPE film was found to be stable up to 4.6 V as shown in Supporting Information: Figure S6. Thus, the high oxidation stability of the SIC-SPE enables its use together with high-voltage cathode materials for ASSBs.

Owing to the promising properties of the SIC-SPE, solid-state electrochemical cells consisting of $\text{LiNi}_{0.7}\text{Co}_{0.15}\text{Mn}_{0.15}\text{O}_2$ (NCM) + SIC-SPE/SIC-SPE film/Li metal were fabricated through the process illustrated in Supporting Information: Figure S7a. The cathode slurry consisting of NCM and SIC-SPE was first blade-cast on an Al foil and dried at 130°C. The electrolyte slurry was then cast directly onto the cathode surface. This fabrication process can provide good interfacial contact between the cathode and electrolyte layers (Supporting Information: Figure S7b) and can be readily scaled up for mass production. As summarized in Supporting Information: Figure 2D,E, we could easily fabricate SIC-SPE cells with an impressive electrochemical performance at 25°C: 163.0, 146.5, 125.5, 95.4, and 55.8 mAh g⁻¹ at 0.1, 0.2, 0.5, 1.0, and 2.0 C, respectively. Thus, it is practically meaningful to compare the capacity values of SIC-SPE cells with a control cell, which has the same configuration, except for replacing SIC-SPE with LPSCl ($\text{Li}_6\text{PS}_5\text{Cl}$). Surprisingly, regardless of the σ of LPSCl being almost 10 times higher than that of SIC-SPE (SIC-SPE: $0.2 \times 10^{-3} \text{ S cm}^{-1}$, LPSCl: $2.2 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C), both discharge capacity and rate capability of the LPSCl cell were similar to those of the SIC-SPE cell. We performed a digital-twin-driven micro-structural analysis of both composite cathodes to unravel this interesting phenomenon.

Once the digital twin composite electrodes are formed, as shown in Figure 3, the microstructural and conductive properties of the corresponding electrodes

can be quantified and compared. More specifically, the volume fraction and effective ionic conductivity of SEs are compared first, and then the contact area between NCM AMs and each SE is discussed later. As expected, the SIC-SPE possesses a slightly higher volume fraction than the LPSCl (SIC-SPE: 32.1%, LPSCl: 26.1%) because of the lower density of the SIC polymer and additional binder volume for the LPSCl electrode (Figure 3A,B). In addition, the SIC-SPE electrode showed a lower tortuosity factor of 1.08 than the LPSCl electrode (1.31) (Supporting Information: Figure S8). In contrast to the uniform and continuous ion pathways within the SIC-SPE electrode, the LPSCl electrode has a more tortuous ionic pathway owing to the void between the SEs and the additional insulating binder phase. To combine these two parameters in the composite electrode, the effective ionic conductivity (σ_{eff}) was simulated as shown in Figure 3C. As a result, the calculated σ_{eff} values of the SIC-SPE and LPSCl electrodes were $2.9 \times 10^{-5} \text{ S cm}^{-1}$ and $4.3 \times 10^{-5} \text{ S cm}^{-1}$, respectively, where the σ_{eff} of the LPSCl-based electrode was still high. However, it should be emphasized that the σ_{eff} of the LPSCl electrode is largely reduced to only 1.9% of the intrinsic σ of LPSCl, while the σ_{eff} of the SIC-SPE electrode maintains 14.3% of the intrinsic σ of SIC-SPE owing to the better percolation pathway. Additionally, considering the importance of the intimate contact area between AMs and SEs for ASSB performance, their contact areas are calculated as the coverage ratio (i.e., the interfacial contact area divided by the total surface area of the AMs). Owing to the polymeric properties of the SIC-SPE, the SIC-SPE electrode showed 68.1% coverage, while the LPSCl contacted only 38.8% of the total AM surface (Figure 3D,E). All our simulation data highlight the structural advantages of the SIC-SPE within the composite electrode.

To verify the structural advantages of the SIC-SPE, we built digital-twin-based electrochemical battery models for the SIC-SPE and LPSCl cells as shown in Figure 4. The ion flux at the last moment of 0.1 C discharge in each electrode was calculated based on the virtual 3D electrode structure, and the results are shown in Figure 4B,F. A low ion flux flowed uniformly to the well-distributed SE in the SIC-SPE-based electrode. However, in the LPSCl electrode, locally concentrated ion flux was observed, implying a high overpotential for Li transport. Figure 4C,G present surface overpotentials of AMs in each electrode, which indicates that the lithiation reaction occur on the surface of AMs during a discharge process. In the SIC-SPE electrode, the surface overpotential was observed on most of the AMs up to the periphery of the current collector, whereas in the LPSCl electrode, it was observed on limited AMs around the

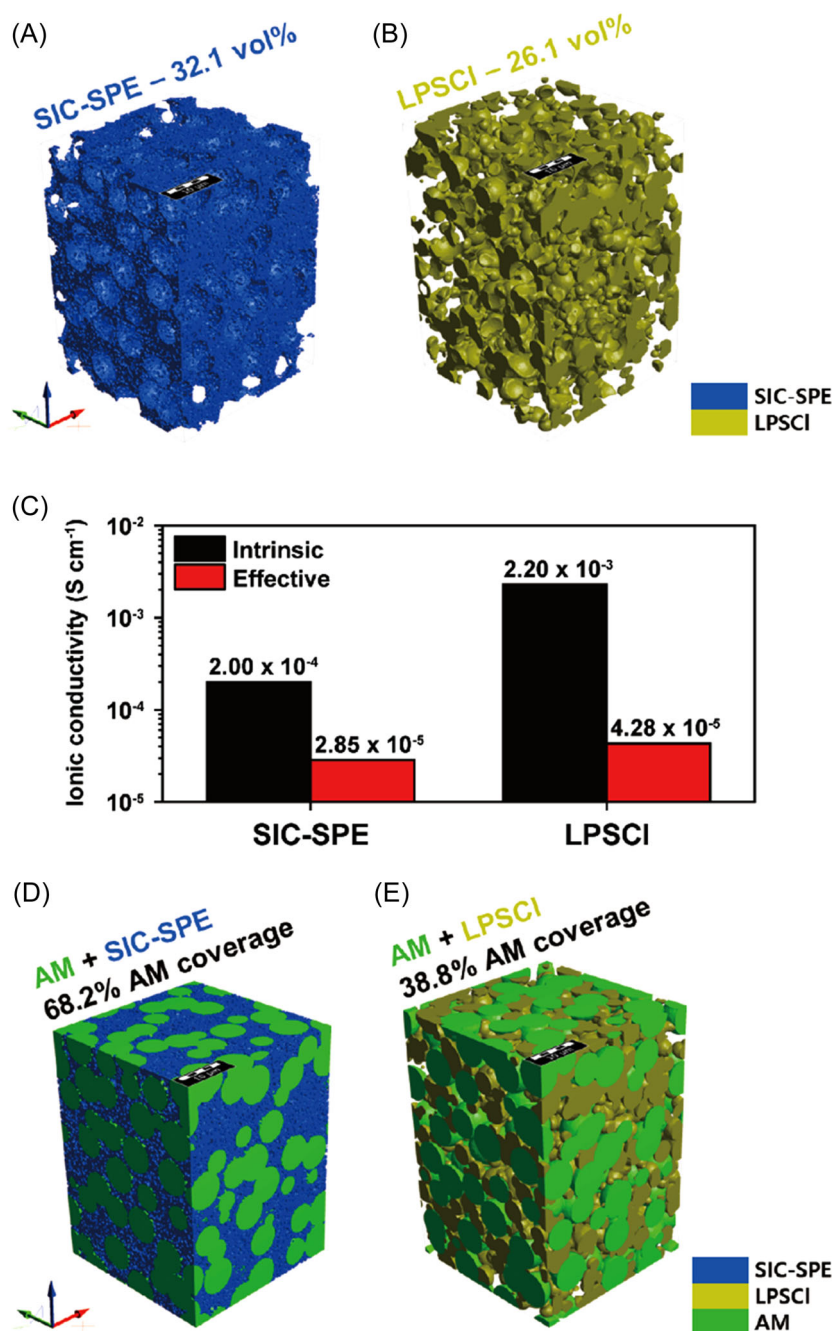


FIGURE 3 Digital-twin-driven 3D electrode structures and their simulated properties. Volume fractions of (A) SIC-SPE and (B) LPSCI ($\text{Li}_6\text{PS}_5\text{Cl}$) phases within the electrode. (C) Intrinsic ionic conductivities of SIC-SPE film and LPSCI pellet and calculated effective ionic conductivities of each electrode with SIC-SPE or LPSCI. Overall 3D structures of (D) SIC-SPE electrode and (E) LPSCI electrode with AM coverage ratios. SIC-SPE, single-ion conducting solid polymer electrolyte.

electrode/electrolyte interface. In addition, when the surface area of the AMs on which the surface overpotential occurred was compared, the AMs at the SIC-SPE electrode showed a wider surface area than the LPSCI electrode. The ion flux and surface overpotential results imply that the SIC-SPE electrodes are advantageous for electrode reactions owing to their well-connected percolation pathway and large AM/SE

interfacial area. These positive factors lead to higher lithiation states across the SIC-SPE electrodes as shown in Figure 4D,H.

Thus, these analysis results strongly suggest that the SIC-SPE is structurally advantageous in composite electrodes for ASSB applications, regardless of its low intrinsic ionic conductivity. In this sense, we need to explore new SIC-SPE materials with higher ionic conductivities while

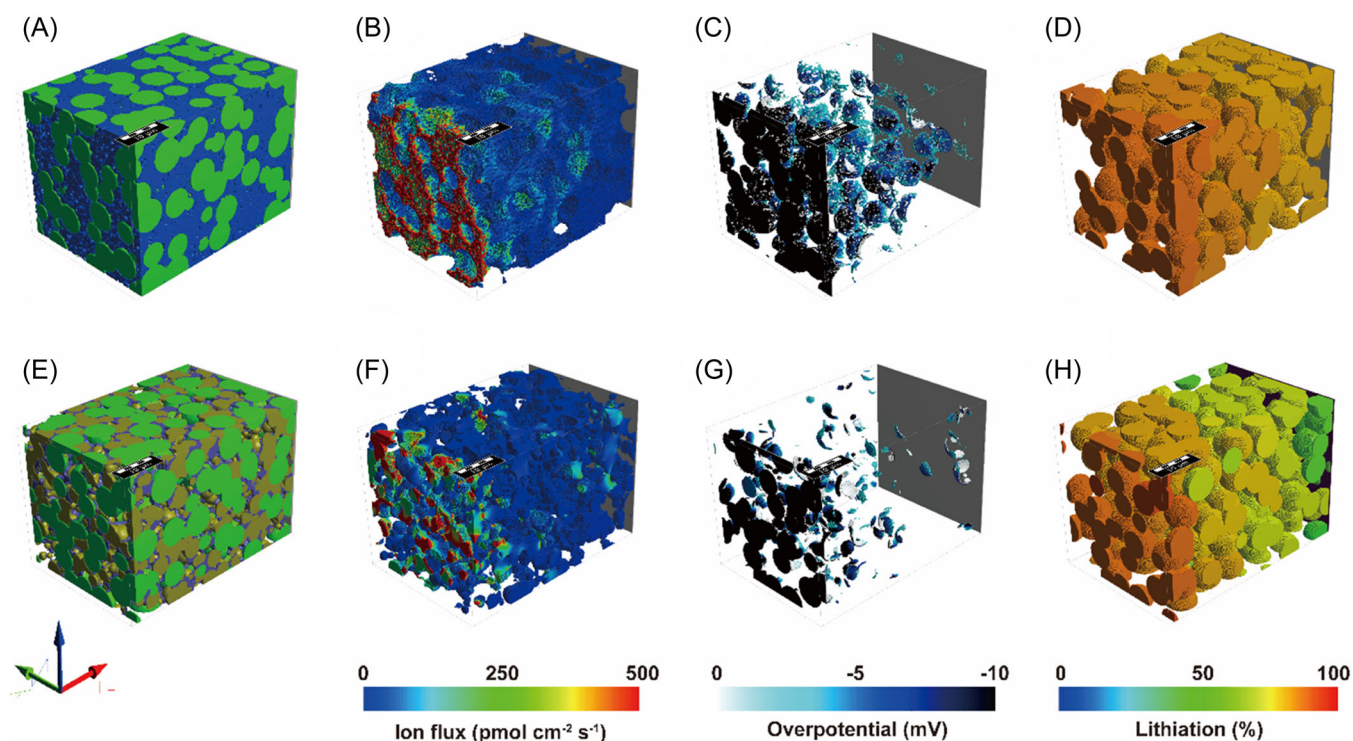


FIGURE 4 Digital-twin-based electrochemical battery models for (A) SIC-SPE and (E) LPSCI cell. Ion flux of (B) SIC-SPE electrode and (F) LPSCI electrode, surface overpotential of AMs of (C) SIC-SPE electrode and (G) LPSCI electrode, and lithiation state of (D) SIC-SPE electrode and (H) LPSCI electrode at the last moment of 0.1 C discharge. AM, active material; SIC-SPE, single-ion conducting solid polymer electrolyte.

maintaining the elasticity and softness of polymers. However, at the same time, the structural parameters such as volume fraction, tortuosity factor, and contact area, extensively dealt with in this work²⁰—should be carefully analyzed and controlled experimentally using digital-twin simulation techniques. Finally, we anticipate that these efforts will improve the shortcomings of SIC-SPEs for innovative advances in ASSBs.

3 | CONCLUSION

We investigated the pivotal role of SIC-SPEs in solid-state composite electrodes with a sulfonated tetrafluoroethylene copolymer containing only Li^+ ions. Despite the SIC-SPE having an ionic conductivity of one order lower than the control electrolyte, LPSCI (SIC-SPE: $0.2 \times 10^{-3} \text{ S cm}^{-1}$, LPSCI: $2.2 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C), the SIC-SPE composite electrode could deliver an impressive discharge capacity and rate capability at room temperature, which are comparable to those of the LPSCI composite electrode. To understand the significant performance of the SIC-SPE electrode, a digital-twin-driven simulation was conducted to compare the structural and electrochemical properties of the SIC-SPE and LPSCI electrodes. A slightly higher volume

fraction, a less tortuous single-ion conduction phase (lower tortuosity), and a much higher contact area between AMs and SEs are observed in the SIC-SPE electrode. With the same amount (wt%) of SE, the SIC-SPE could improve the effective ionic conductivity and provide a larger electrochemically active surface within the composite electrode. Thus, when designing and optimizing composite electrodes for ASSB, forming a well-structured electrolyte phase like SIC-SPE is as important as finding SE with high ion conductivity. It should also be stressed that digital-twin modeling and simulation are essential for understanding and controlling the solid-state composite electrode and corresponding cells.

ACKNOWLEDGMENTS

J. Lee, S. Byun, and H. Lee contributed equally to this work. This work was supported by the Development Program of Core Industrial Technology (No. 20012326) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea) and the National Research Foundation of Korea (NRF-2022M3J1A1054326) funded by the Ministry of Science and ICT. Also, this work was also supported by the BK21 FOUR program through the National Research Foundation (NRF) funded by the Ministry of Education of Korea.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION

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

How to cite this article: Lee J, Byun S, Lee H, et al. Digital-twin-driven structural and electrochemical analysis of Li⁺ single-ion conducting polymer electrolyte for all-solid-state batteries. *Battery Energy.* 2023;2:20220061. doi:10.1002/bte2.20220061