# Ultrathin Superhydrophobic Coatings for Air-Stable Inorganic Solid Electrolytes: Toward Dry Room Application for All-Solid-State Batteries

Kyu Tae Kim, Jehoon Woo, Young-Soo Kim, Sihyeon Sung, Changhyun Park, Chanhee Lee, Young Joon Park, Hyun-Wook Lee, Kyusung Park, and Yoon Seok Jung\*

Inorganic solid electrolytes (SEs), such as sulfides and halides, are crucial for developing practical all-solid-state batteries (ASSBs) owing to their high ionic conductivities and mechanical sinterabilities. However, their sensitivity to humid air necessitates stringent dry-room conditions during processing, which increases production costs. This study demonstrates that ultrathin ( $\approx$ 5 nm) superhydrophobic polydimethylsiloxane (PDMS) or fluorinated PDMS (F-PDMS) protective layers can enhance the stability of air-sensitive sulfide (Li<sub>6</sub>PS<sub>5</sub>Cl (LPSCl)) and halide (Li<sub>25</sub>Zr<sub>05</sub>In<sub>05</sub>Cl<sub>6</sub>) SEs in ASSBs. The (F)-PDMS coatings are applied using a scalable, straightforward vapor-phase deposition process, achieving high Li<sup>+</sup> conductivity retention (92%, from 2.5 to 2.3 mS cm<sup>-1</sup> at 30 °C). The protective layers effectively inhibit LPSCI degradation under practically relevant dry room conditions (dew point of -50 °C or -10 °C): e.g., from 2.3 to 0.97 mS cm<sup>-1</sup> for PDMS-coated LPSCI versus from 2.5 to 0.57 mS cm<sup>-1</sup> for bare LPSCI. Surprisingly, the superhydrophobic coatings facilitate the recovery of Li<sup>+</sup> conductivity via vacuum heat treatment. This new phenomenon, known as regeneration, is achieved by the facile elimination of adsorbed water. Furthermore, the regenerated (F)-PDMS-coated LPSCI demonstrates significant performance in NCM||Li-In ASSB cells. These findings suggest that superhydrophobic (F)-PDMS coatings are a promising solution for practical all-solid-state technologies.

1. Introduction

All-solid-state batteries (ASSBs) employing inorganic solid electrolytes (SEs) have the potential to deliver increased safety and superior energy density compared with traditional lithium-ion batteries.<sup>[1–4]</sup> For practical applications, SEs should exhibit high ionic conductivities of at least  $\approx 1 \text{ mS cm}^{-1}$  at room temperature (RT) and possess deformable mechanical properties that enable scalable cold-pressing fabrication.<sup>[5]</sup> Sulfide (e.g.,  $Li_{6-v}PS_{5-v}X_{1+v}$  (X = Cl, Br; y = 0.0– 0.5): 1-10 mS cm<sup>-1</sup>)<sup>[6,7]</sup> and halide materials (e.g.,  $Li_3MX_6$  or  $Li_2MX_6$  (M = Y, Zr, In, and Sc; X = Cl, Br): 0.51– 1.7 mS cm<sup>-1</sup>, and LiMOCl<sub>4</sub> (M = Ta, Nb): maximum  $\approx 10 \text{ mS cm}^{-1}$  meet these requirements and have been extensively studied. However, these SE materials are unstable in atmospheric air<sup>[9,13-17]</sup> and undergo degradation as a result of hydrolysis as well as hydration reactions.<sup>[14,17]</sup> Specifically, sulfide SEs react with water molecules, releasing toxic H<sub>2</sub>S gases. Although halide SEs eliminate H<sub>2</sub>S concerns, they still degrade in atmospheric air.[9,18-20] These SEs can adsorb and react with

K. T. Kim, J. Woo, Y. J. Park, Y. S. Jung Department of Chemical and Biomolecular Engineering Yonsei University 03722 Seoul, Republic of Korea E-mail: yoonsjung@yonsei.ac.kr Y.-S. Kim, S. Sung, K. Park Next Generation Development Team Samsung SDI R&D Center 16678 Suwon, Republic of Korea C. Park, C. Lee, H.-W. Lee School of Energy and Chemical Engineering Ulsan National Institute of Science and Technology 44919 Ulsan, Republic of Korea

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/aenm.202301600

#### DOI: 10.1002/aenm.202301600

moisture, decomposing into hydrated compounds of  $MCl_3^{\bullet}H_2O$  and  $LiCl^{\bullet}H_2O$  or hydrated forms (e.g.,  $Li_3MCl_6^{\bullet}H_2O$ ).

In laboratory-scale research, air-sensitive SE is processed in glove boxes filled with inert gases such as Ar. However, for practical applications, SEs and ASSBs must be processed and manufactured under dry room conditions, where minimal humidity is unavoidable.<sup>[21]</sup> Specifically, conventional LIB dry room conditions have a dew point of  $\approx$ 40 °C.<sup>[22]</sup> Unfortunately, under these conditions, sulfide SEs degrade and lose a significant percentage of their original conductivity (23.5%) within just an hour.<sup>[23]</sup> As a result, more stringent dry-room conditions, such as –50 to –60 °C, are necessary but result in a significant increase in costs. Thus, understanding the degradation mechanisms of SEs and designing air-stable SEs are critical for implementing all-solid-state technologies.



Figure 1. Schematic of vapor-phase deposition of (F)-PDMS (poly(dimethylsiloxane) (PDMS) or fluorinated PDMS) on the surfaces of inorganic SE powders, including sulfide (Li<sub>6</sub>PS<sub>5</sub>Cl) and halide SEs (Li<sub>2.5</sub>Zr<sub>0.5</sub>In<sub>0.5</sub>Cl<sub>6</sub>).

Several design strategies for sulfide SEs have been identified to improve air stability.<sup>[24,25]</sup> One approach involves combining sulfide SEs with adsorbents.<sup>[26-29]</sup> Hayashi et al. demonstrated that metal oxide  $M_x O_v$  (M = Fe, Zn, and Bi) nanoparticles effectively adsorb H<sub>2</sub>S gas from sulfide SEs.<sup>[26]</sup> Composite SEs composed of Li<sub>3</sub>PS<sub>4</sub> and M<sub>x</sub>O<sub>y</sub> prepared using a simple ball-milling process exhibited suppressed H<sub>2</sub>S evolution but only a marginal improvement in Li<sup>+</sup> conductivity retention. Lee et al. used a zeolite as an additive for Li<sub>6</sub>PS<sub>5</sub>Cl (LPSCl), where the zeolite acted as a scavenger of both toxic H<sub>2</sub>S gas and moisture.<sup>[29]</sup> Further, developing new compositions or fine-tuning existing compositions with chemically stable bonding based on the hard and soft acids and bases (HSAB) theory has been effective in improving the air stability of sulfide SEs.<sup>[4,30-35]</sup> The substitution of the hard acid  $P^{5+}$  with soft acids, such as  $Sn^{4+},\,As^{5+},\,and$ Sb5+, results in enhanced chemical stability. Li3 833 Sn0 833 As0 166 S4 demonstrated a marginal decrease in Li<sup>+</sup> conductivity from 1.39 to 0.995 mS cm<sup>-1</sup> after air exposure. In comparison, conventional Li<sub>3</sub>PS<sub>4</sub> experienced a drop in Li<sup>+</sup> conductivity of more than an order of magnitude.<sup>[30]</sup> Our group developed phosphorus-free sulfide SEs using cost-effective and non-toxic elements while maintaining excellent air stability: Sb-substituted Li<sub>4</sub>SnS<sub>4</sub> (e.g.,  ${\rm Li}_{3.85}Sn_{0.85}Sb_{0.15}S_4).^{[31]}$  However, the stability benefits achieved using soft acids (i.e., Sn, As, and Sb) are counterbalanced by electrochemical reduction stability, cost-effectiveness, and increased density. Third, surface treatments have been proposed to improve the air stability of sulfide SEs, which could align with advancements in lithium-ion and lithium-metal batteries.[36,37] When LP-SCl is exposed to pure oxygen, it forms a 50 nm thick oxysulfide nanolayer, effectively suppressing air-induced degradation.<sup>[38]</sup> Considering surface treatments can add functionality without compromising the original bulk properties, various strategies for creating a protective coating layer on SEs have been explored.[38-45]

Polydimethylsiloxane (PDMS) has several advantages as a coating material, including low surface tension, multiscale structures with high stability, cost-effectiveness, and versatile deposition methods.<sup>[46,47]</sup> Particularly, PDMS enables vapor-phase deposition, which is inexpensive, rapid, solvent-free, and easy to scale, making it highly attractive for creating superhydrophobic coatings.<sup>[48,49]</sup> As a result, PDMS coatings have been investigated in various research fields, including membranes, metal–organic frameworks, and LIBs;<sup>[48–50]</sup> however, their application in SEs and ASSBs is unexplored.

Based on forgoing, superhydrophobic PDMS or fluorinated PDMS (F-PDMS) coatings are applied using scalable vapor-phase deposition to achieve air-stable sulfide or halide SEs. The ultrathin (5 nm) coating layers provide excellent retention in Li<sup>+</sup> conductivity of LPSCl, up to 92% (from 2.5 to 2.3 mS cm<sup>-1</sup> at 30 °C). Furthermore, these superhydrophobic layers effectively suppress air-induced degradation in both humid atmospheres and practically relevant dry room environments. Remarkably, when sulfide SEs degraded due to exposure to dry room air or humidity and were later regenerated by heat treatment (HT) under vacuum, the regeneration efficiency (or retention of Li<sup>+</sup> conductivity) was significantly improved by the use of superhydrophobic coatings (204% vs 1298%), as demonstrated for the first time. Complementary analysis revealed that the improved performance was due to the significantly reduced uptake of H<sub>2</sub>O by the superhydrophobic coating. Finally, the feasibility of using the PDMSor F-PDMS-coated LPSCl for capacity retention in ASSB cells was successfully demonstrated. Furthermore, the adaptability of the vapor-phase deposition for superhydrophobic coatings was demonstrated by its application to the halide SE Li<sub>25</sub>Zr<sub>05</sub>In<sub>05</sub>Cl<sub>6</sub> (LZIC).

#### 2. Results and Discussion

Superhydrophobic PDMS coatings were applied to sulfide (LPSCl) or halide (LZIC) SE powders through vapor-phase deposition, as shown in **Figure 1**. At high temperatures (e.g., 243 °C), PDMS decomposes, and the vaporized fragments are deposited onto the surfaces of the SEs, forming superhydrophobic coating layers. Based on gel permeation chromatography (GPC) measurements, the number-average molecular weight ( $M_n$ ) of PDMS used in this study was determined to be 2.0 × 10<sup>4</sup> (Figure S1 and Table S1, Supporting Information). F-PDMS was also fabricated to achieve higher hydrophobicity using 1H, 1H, 2H, 2H-perfluorododecyltriethoxysilane as a PDMS cross-linker as per (Figure S2, Supporting Information).<sup>[51]</sup>

The samples—bare LPSCl, PDMS-coated LPSCl (referred to as "P-LPSCl"), and F-PDMS-coated LPSCl (referred to as "FP-LPSCl")—were characterized using cryogenic high-resolution transmission electron microscopy (cryo-HRTEM), X-ray photoelectron spectroscopy (XPS), and electrochemical impedance spectroscopy (EIS) measurements (**Figure 2**). The cryo-HRTEM images (Figures 2a–c) reveal amorphous layers with a thickness www.advancedsciencenews.com

CIENCE NEWS



Figure 2. Characterization of LPSCI, P-LPSCI, and FP-LPSCI. Cryo-TEM images of a) LPSCI, b) P-LPSCI, and c) FP-LPSCI. Si 2p XPS spectra of d) LPSCI, e) P-LPSCI, and f) FP-LPSCI. Nyquist plots of Ti|SE|Ti symmetric cells at 30 °C for g) LPSCI, h) P-LPSCI, and i) FP-LPSCI.

of ≈5 nm on P-LPSCl and FP-LPSCl surfaces, significantly different from the lattice fringes with a d-spacing value of 0.39 nm, corresponding to the  $\{220\}$  plane of the Li<sub>6</sub>PS<sub>5</sub>Cl crystal. X-ray diffraction (XRD) confirmed that the original crystal structure of Li<sub>6</sub>PS<sub>5</sub>Cl was preserved after the coating process (Figure S3, Supporting Information). The XPS spectra (Figure 2d-f) confirm the presence of the coating layers, consistent with the cryo-HRTEM results. Si 2p signals are detected at 102.0 eV in P-LPSCl and FP-LPSCl, but not in bare LPSCl. Moreover, a significant reduction in the Si 2p signal for the coated LPSCl after 600 s etching substantiates the ultrathin PDMS coating layers (Figure S4, Supporting Information). The clear F-1s XPS spectrum of FP-LPSCl confirmed the presence of a fluorine moiety (Figure S5, Supporting Information). Interestingly, the evolution of the bridging sulfur (P-[S]<sub>n</sub>-P), PO<sub>x</sub>S<sub>y</sub>, and P<sub>2</sub>S<sub>5</sub> was observed in the coated LPSCl samples (Figure S6, Supporting Information). In a control experiment, LPSCl was subjected to HT under vacuum at 243 °C without the presence of any coating precursor (PDMS or F-PDMS). Similar types were observed in the coated samples after HT (Figure S7, Supporting Information), possibly due to surface sulfur loss and/or reaction with traces of oxygen.<sup>[52]</sup> The weight fractions of the coating layers for P-LPSCl and FP-LPSCl were determined using thermogravimetric analysis (TGA) measurements to be 1–2 wt.% (Figure S8, Supporting Information).

Figure 2g–i presents the Nyquist plots of Ti|SE|Ti Li<sup>+</sup>-blocking symmetric cells at 30 °C for LPSCl, P-LPSCl, and FP-LPSCl. The equivalent circuit model and the fitted results are also provided in Figure S9 and Table S2 (Supporting Information). For LPSCl, a simple straight line was observed, indicating a negligible contribution of the grain boundary resistance, and the corresponding Li<sup>+</sup> conductivity was 2.5 mS cm<sup>-1</sup>. In contrast, small semicircles appear for P- and FP-LPSCl, indicating the development of grain boundary resistance, attributed to the coating layers and byproducts originating from the vacuum HT process. However, the decrease in Li<sup>+</sup> conductivity caused by the coating is acceptable: 2.3 and 2.0 mS cm<sup>-1</sup> for P- and FP-LPSCl, respectively, corresponding to 92% and 80% retention. Particularly, the 92%





**Figure 3.** Air stability results of sulfide (LPSCI, P-LPSCI, and FP-LPSCI) and halide (LZIC, P-LZIC, and FP-LZIC) SEs. a) Nyquist plots of Ti|SE|Ti symmetric cells at 30 °C for LPSCI, P-LPSCI, and FP-LPSCI before and after dry-room exposure (dew point of -50 °C for 72 h) at 30 °C. b) Corresponding Li<sup>+</sup> conductivities and their retention. c) Nyquist plots of Ti|SE|Ti symmetric cells at 30 °C for LZIC, P-LZIC, and FP-LZIC before and after dry-room exposure (dew point of -50 °C for 72 h) at 30 °C. corresponding Li<sup>+</sup> conductivities and their retention are also displayed in (b). d) Schematic illustrating the protective role of superhydrophobic (F)-PDMS coatings against moisture.

retention of Li<sup>+</sup> conductivity is among the highest reported to date (Table S3, Supporting Information), attributed to the ultrathin scale ( $\approx$ 5 nm) of the coating layers and the benefits of the solvent-free process.

CIENCE NEWS

The air stability of LPSCl, P-LPSCl, and FP-LPSCl was evaluated by storing the powder samples in a dry room with a dew point of -50 °C (relative humidity 0.2%) for 72 h. Figure 3a shows a series of Nyquist plots of Ti|SE|Ti cells for LPSCl, P-LPSCl, and FP-LPSCl before and after exposure. All the samples experienced a significant increase in impedance after being exposed. However, P-LPSCl and FP-LPSCl exhibit significantly smaller impedance increases than bare LPSCl. The corresponding Li<sup>+</sup> conductivities and their retention before and after exposure are summarized in Figure 3b. The Li<sup>+</sup> conductivity of LPSCl dropped from 2.5 to 0.57 mS cm<sup>-1</sup> after exposure, corresponding to a 23% retention. In contrast, the Li<sup>+</sup> conductivity decrease for P- and FP-LPSCl was from 2.3 to 0.97 mS cm<sup>-1</sup> and from 2.0 to 0.98 mS cm<sup>-1</sup>, respectively, representing 42% and 49% retention. Notably, the Li<sup>+</sup> conductivity values for the coated LPSCl after exposure were higher than those for the air-exposed bare LPSCl (0.97 or 0.98 vs 0.57 mS cm<sup>-1</sup>). The conductivity values of the samples are summarized in Table S4 (Supporting Information). Furthermore, P-LPSCl and FP-LPSCl exhibit smaller amount of H<sub>2</sub>S generation compared to LPSCl (Figure S10, Supporting Information).

A comprehensive study of the evolution and degradation of LP-SCl upon air exposure was conducted using bare LPSCl, P-LPSCl, and FP-LPSCl. Time-resolved EIS, XRD, Raman, and XPS measurements were performed while the samples were subjected to harsh conditions with a dew point of -10 °C (relative humidity 9%) for 72 h. Samples were collected and analyzed at 24 h intervals during the exposure period. The coated LPSCl outperformed the bare LPSCl after up to 24 h of exposure, consistent with the

results obtained at a dew point of -50 °C. Notably, after 48 h of exposure, FP-LPSCl outperformed P-LPSCl and bare LPSCl, attributed to the increased hydrophobicity of F-PDMS compared to PDMS, effectively inhibiting the intrusion of H<sub>2</sub>O into the bulk LPSCl. However, after 72 h of exposure, all the samples exhibited large semicircles, indicating severe degradation (Figure S11, Supporting Information). Time-resolved XRD and Raman spectra exhibited similar behaviors (Figures S12 and S13, Supporting Information). The time-resolved XPS spectra in Figures S14-S16 (Supporting Information) revealed complex evolution behaviors. In particular, pinpointing the effects of air exposure is challenging because the bridging sulfur species P-[S]<sub>n</sub>-P, PO<sub>x</sub>S<sub>y</sub>, and P<sub>2</sub>O<sub>5</sub> are byproducts of both air exposure and vacuum HT. However, SO<sub>4</sub><sup>2-</sup> is the only form generated solely by air exposure and can be used to predict the rate of air-induced degradation. The peak intensity of SO42- for bare LPSCl increased dramatically during air exposure compared to that of the coated LPSCl samples. After 72 h of exposure, the relative area ratio of the  $SO_4^{2-}$  to  $PS_4^{3-}$ peaks for LPSCl was 0.4, three times higher than that of P-LPSCl and FP-LPSCl.

The vapor-phase deposition of superhydrophobic PDMS and F-PDMS for the halide SE LZIC was also verified.<sup>[53]</sup> After 72 h exposure in a dry room with a dew point of -50 °C, the Li<sup>+</sup> conductivities of PDMS-coated LZIC (referred to as "P-LZIC") and F-PDMS-coated LZIC (referred to as "FP-LZIC") decreased from 0.71 to 0.18 and from 0.87 to 0.27 mS cm<sup>-1</sup> at 30 °C, representing 25% and 31%, respectively. These values were higher than that for the exposed bare LZIC (from 1.4 to 0.13 mS cm<sup>-1</sup>), corresponding to 9.3% (Figure 3b,c). Moreover, under harsher exposure conditions with a dew point of -10 °C, the Li<sup>+</sup> conductivity retention followed the order FP-LZIC >P-LZIC >LZIC (Figure S17, Supporting Information). These results are consistent with the observations of LPSCI.

/onlinelibrary.wiley.com/term

and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons.

ADVANCED SCIENCE NEWS \_\_\_\_\_ www.advancedsciencenews.com

The versatility of superhydrophobic coatings can be attributed to two key features. First, PDMS can be easily vaporized under mild vacuum HT conditions, preventing thermal damage to the substrate materials. Second, while sulfide and halide SEs undergo side reactions or dissolution when exposed to organic solvents,<sup>[9,54–56]</sup> vapor-phase deposition is solvent-free. In summary, the significant improvement in air stability achieved by vapor-phase-derived PDMS or F-PDMS coatings for LPSCI and LZIC demonstrated the effectiveness of the ultrathin superhydrophobic layer in preventing H<sub>2</sub>O-intrusion, as shown in Figure 3d.

Considering that the components of ASSBs require drying under vacuum HT conditions before cell assembly, similar to conventional LIB manufacturing, the properties of SEs exposed to a dry room and then dried under vacuum HT conditions directly impact the performance of ASSB cell products.<sup>[14,57]</sup> In this context, the drying process is referred to as "regeneration". The regeneration abilities of humid-atmosphere-exposed LPSCl, P-LPSCl, and FP-LPSCl were assessed, with the results shown in Figure 4. After exposing the powder samples to saturated humid Ar at 60 °C for 6 h (hereafter referred to as "humid atmosphere"), they were subjected to HT at 150 °C under vacuum for 12 h (Figure 4a). Hereafter, LPSCl, P-LPSCl, and FP-LPSCl exposed to a humid atmosphere are denoted as Exp-LPSCl, Exp-P-LPSCl, and Exp-FP-LPSCl, respectively, and those regenerated by vacuum HT are denoted as HT-LPSCl, HT-P-LPSCl, and HT-FP-LPSCl, respectively. The Nyquist plots of the Ti|SE|Ti cells at 30 °C for the samples exposed to the humid atmosphere in Figure S18 (Supporting Information) show severe degradation with no noticeable differences in the amplitude of the semicircles. The Li<sup>+</sup> conductivities partially recovered after the vacuum HT regeneration process (Figure 4b). Surprisingly, both HT-P-LPSCl and HT-FP-LPSCl demonstrated a substantial recovery in Li<sup>+</sup> conductivity compared to HT-LPSCl (3.7  $\times$  10<sup>-6</sup> and 4.2  $\times$  10<sup>-6</sup> S cm<sup>-1</sup>, respectively vs  $6.3 \times 10^{-7}$  S cm<sup>-1</sup>).

To elucidate the underlying mechanism of these differences, complementary analyses were performed using Raman (Figures 4c-e; Figures S19 and S20, Supporting Information) and TGA with mass spectrometry (TGA-MS, Figures 4f-h) measurements. While the pristine samples (without humid-atmosphere exposure) exhibited PS43- stretching near 425 cm<sup>-1</sup>, humidatmosphere exposure resulted in a blueshift to 418 cm<sup>-1</sup>, indicating the formation of oxysulfide bonds via hydrolysis (Figure 4ce).<sup>[13,14,58]</sup> Furthermore, weak signals near 3560 cm<sup>-1</sup> were detected, indicating the formation of a hydroxyl moiety (Figure S19, Supporting Information).<sup>[59]</sup> According to these findings, all samples underwent both hydrolysis and hydration reactions. Following vacuum HT, LPSCl showed a further blue shift in the oxysulfide bond from 418 to 415 cm<sup>-1</sup>, indicating additional side reactions during the regeneration process (Figure 4c). In contrast, for HT-P-LPSCl and HT-FP-LPSCl, the oxysulfide bonding did not exhibit any shifts, implying the absence of additional side reactions (Figure 4d,e), possibly due to the varying levels of recovery effectiveness of Li+ conductivity after vacuum HT.

The TGA-MS profiles under an Ar flow for Exp-LPSCl, Exp-P-LPSCl, and Exp-FP-LPSCl are displayed in Figures 4f–h, respectively. As the LPSCl and (F)-PDMS coating themselves experience weight loss during TGA measurement (Figure S8, Sup-

porting Information), the TGA profiles shown in Figures 4f-h were obtained by excluding the weight contribution of the coatings. This exclusion was achieved by subtracting the TGA data presented in Figure S8 (Supporting Information). All samples showed significant evolution of H<sub>2</sub>O and H<sub>2</sub>S significantly near 200 °C, along with smaller amounts near 300 °C. The weight losses of Exp-LPSCl, Exp-P-LPSCl, and Exp-FP-LPSCl from 30 to 220 °C were similar at 31.3%, 30.2%, and 31.5%, respectively. However, the weight loss results should be considered in conjunction with weight gain during humid atmospheric exposure. In particular, LPSCl had the smallest weight gain after humid-atmosphere exposure (Exp-LPSCl), +33.5 wt.%, whereas the weight gains for Exp-P-LPSCl and Exp-FP-LPSCl were similar: +39.0 and +39.4 wt.%, respectively (Figure S21, Supporting Information). When exposed to a humid atmosphere, the weight gain by H<sub>2</sub>O adsorption via the hydration reaction and weight loss by H<sub>2</sub>S evolution counteracted each other. Notably, based on the TGA-MS and weight change results, more H<sub>2</sub>S evolution occurred for LPSCl than for P-LPSCl or FP-LPSCl during humidatmosphere exposure. Vacuum HT causes dehydration and removal of residual moisture. However, the regenerated LPSCl, i.e., HT-LPSCl, still showed significant evolution of H<sub>2</sub>O and H<sub>2</sub>S near 200 °C with 7.0 wt.% weight loss from 30 to 220 °C. In sharp contrast, HT-P-LPSCl and HT-FP-LPSCl showed marginal mass signals of H<sub>2</sub>O and H<sub>2</sub>S near 200 °C with remarkably lower weight losses of 1.1 and 2.2 wt.%, respectively, indicating that adsorbed H<sub>2</sub>O was effectively eliminated by vacuum HT, consistent with much higher weight losses during vacuum HT for the coated LPSCl (31.7 and 31.0 wt.% for P-LPSCl and FP-LPSCl, respectively) than for bare LPSCl (26.3 wt.%) (Figure S21, Supporting Information).

These results suggest that the (F)-PDMS coatings enabled the effective removal of adsorbed H<sub>2</sub>O and the recovery of Li<sup>+</sup> conductivity via vacuum HT, as illustrated in Figure 4i,j. For the uncoated LPSCl, H<sub>2</sub>O was adsorbed onto the large surface area of LPSCl after air exposure. During vacuum HT, the adsorbed H<sub>2</sub>O induces additional reactions. In contrast, for P-LPSCl and FP-LPSCl, the superhydrophobic coatings prevent the direct adsorption of H<sub>2</sub>O onto LPSCl, thereby avoiding any additional side reactions. Moreover, the low surface energy of (F)-PDMS facilitated the easy removal of adsorbed H<sub>2</sub>O via a moderate-vacuum HT process.<sup>[46]</sup> This efficient removal of moisture contributed to the improved performance of the coated LPSCl samples, demonstrating the efficacy of the (F)-PDMS coatings in improving the stability and conductivity of the SEs. Unfortunately, the regeneration of LZIC by vacuum HT was not successful (Figures S22 and S23, Supporting Information), despite yielding better results with the superhydrophobic coatings than with the bare sample. This may suggest that LZIC may be highly vulnerable to the reaction with water at elevated temperature.<sup>[9,18-20]</sup> As halide SEs demonstrate varying electrochemical and chemical stabilities depending on the central metal and anion,<sup>[60,61]</sup> a further investigation into the regeneration of various type of halide SEs could be an interesting subject that falls within the scope of our future work.

Finally, the dry-room applicability of the (F)-PDMS coatings was evaluated for  $LiNi_{0.90}Co_{0.05}Mn_{0.05}O_2$  (NCM)||Li-In all-solid-state half-cells at 30 °C (**Figure 5**). LPSCl, P-LPSCl, and FP-LPSCl powders were stored in a dry room with a dew point of -50 °C for

SCIENCE NEWS \_\_\_\_

www.advancedsciencenews.com





**Figure 4.** Degradation and regeneration of LPSCI, P-LPSCI, and FP-LPSCI. a) Schematic illustration of degradation and regeneration process of LPSCI, P-LPSCI, and FP-LPSCI. b) Li<sup>+</sup> conductivities for LPSCI, P-LPSCI, and FP-LPSCI after saturated humid-atmosphere-exposure (at 60 °C for 6 h, filled triangle) and after regeneration (by heat treatment at 150 °C under vacuum for 12 h, unfilled circle). Raman spectra before and after exposure to saturated humid atmosphere and after regeneration for c) LPSCI, d) P-LPSCI, and e) FP-LPSCI. TGA-MS results after water exposure and after regeneration for f) LPSCI, g) P-LPSCI, and h) FP-LPSCI. Weight losses at 220 °C are denoted as a cross mark. Schematic illustrating the regeneration behavior i) LPSCI and j) P-LPSCI or FP-LPSCI.

7 days before being regenerated by vacuum HT at 150 °C for 12 h. These powders were then employed as catholytes in ASSB cells. Li<sup>+</sup> conductivities of the regenerated SEs were 0.14, 0.46, and 0.56 mS cm<sup>-1</sup> for LPSCl, P-LPSCl, and FP-LPSCl, respectively. Figure 5a displays the first-cycle charge-discharge voltage profiles of NCM||Li-In half cells at 0.5 C and 30 °C. The NCM electrodes made from LPSCl had an initial discharge capacity of 158 mA

h g<sup>-1</sup>. In contrast, the NCM electrodes fabricated using P-LPSCl and FP-LPSCl have remarkably high initial discharge capacities of 175 and 181 mA h g<sup>-1</sup>, respectively. Notably, the NCM electrodes made from P-LPSCl and FP-LPSCl had lower overpotentials than those from LPSCl, attributed to the excellent retention of Li<sup>+</sup> conductivity after regeneration. The cycling performances and corresponding Coulombic efficiencies of the ASSB cells are

SCIENCE NEWS \_\_\_\_\_ www.advancedsciencenews.com



Figure 5. a) First-cycle charge-discharge voltage profiles of NCM||Li-In all-solid-state half-cells at 0.5C and 30  $^{\circ}$ C, and b) corresponding cycling performance at 0.5C. c) Schematic showcasing the scalable integration of inorganic SEs with superhydrophobic coating layers for large-scale manufacturing of ASLBs.

shown in Figure 5b and Figure S24 (Supporting Information), respectively. A showcase of the scalable application of the (F)-PDMS coating is illustrated in Figure 5c. Under dry-room conditions, the degradation of inorganic SEs by trace amounts of water is inevitable. The (F)-PDMS coatings effectively protect the SE surfaces from water intrusion. Importantly, these coatings aided in the effective recovery of Li<sup>+</sup> conductivity via mild vacuum HT, which has already been incorporated into conventional LIB manufacturing protocols.

#### 3. Conclusion

Using a scalable straightforward vapor-phase deposition method, ultrathin ( $\approx 5$  nm) superhydrophobic protective layers of (F)-PDMS were successfully applied to air-sensitive sulfide (LPSCl) or halide (LZIC) SEs. The Li<sup>+</sup> conductivity retention after coating was impressively high: 92% (from 2.5 to 2.3 mS cm<sup>-1</sup> for P-LPSCl), attributed to the thin coating layer. Significantly, these superhydrophobic coatings effectively suppressed the degradation of LPSCl under practically relevant dry room conditions with a dew point of -50 °C for 72 h: The Li<sup>+</sup> conductivity retentions were 42% and 49% (from 2.3 to 0.97 mS cm<sup>-1</sup> and from 2.0 to 0.98 mS cm<sup>-1</sup>) for P-LPSCl and FP-LPSCl, respectively, compared to 23% (from 2.5 to 0.57 mS cm<sup>-1</sup>) for the bare LPSCl. Under harsh conditions with a dew point of -10 °C, delayed airinduced degradation was confirmed by time-resolved EIS, XRD, XPS, and Raman analyses. Remarkably, the coated LPSCl exhibited significant regeneration ability compared to bare LPSCl, attributed to the easier elimination of adsorbed water from the coated LPSCl, as revealed by the TGA-MS results. When regenerated P- or FP-LPSCl was used in NCM||Li-In ASSB cells, its

superior performance over cells using uncoated LPSCl was confirmed: 175 and 181 mA h g<sup>-1</sup> for P-LPSCl and FP-LPSCl, compared to 158 mA h g<sup>-1</sup> for bare LPSCl. We believe that superhydrophobic (F)-PDMS coatings are a promising solution for improving the performance and stability of ASSBs under real-world conditions.

## 4. Experimental Section

Preparation of Materials: PDMS (viscosity 2250-3570 cSt, Sigma-Aldrich) was used as received. F-PDMS was prepared as described in the previous report.<sup>[51]</sup> After PDMS was dissolved in *n*-heptane, 1H,1H,2H,2H-perfluorodecyltriethoxysilane (PFDTES, 97%, Sigma-Aldrich) and dibutyltin dilaurate (DBTOL, 5%, Sigma-Aldrich) was added with a weight ratio for PDMS/n-heptane/PFDTES/DBTOL of 1:10:0.4:0.005. The resulting mixture was stirred at RT for 12 h. After drying the mixtures at RT overnight, residual solvents were removed by subsequently heating at 120 °C for 12 h. Li argyrodite LPSCI (Li<sub>6</sub>PS<sub>5</sub>Cl) was prepared employing ball-milling and subsequent HT under an Ar atmosphere. After a stoichiometric mixture of Li<sub>2</sub>S (99.9%, Alfa-Aesar), P<sub>2</sub>S<sub>5</sub> (99%, Sigma-Aldrich), and LiCl (99.99%, Sigma-Aldrich) were ball-milled at 600 rpm for 10 h in a  $ZrO_2$  vial with the  $ZrO_2$  balls using Pulverisette 7PL (Fritsch GmbH), HT was conducted at 550 °C for 5 h under Ar atmosphere. LZIC ( $Li_{2.5}Zr_{0.5}In_{0.5}Cl_6$ ) was prepared employing ball-milling and subsequent HT in a fused silica ampoule sealed under vacuum. A stoichiometric mixture of LiCl (99.99%, Sigma-Aldirch), ZrCl<sub>4</sub> (99.99%, Sigma-Aldirch), and InCl<sub>3</sub> (99.99% Alfa-Aesar) was ball-milled at 600 rpm for 10 h using ZrO2 balls, followed by heating at 260 °C for 12 h. (F)-PDMS-coated LPSCI or LZIC were prepared by HT in a fused silica ampoule sealed under vacuum. The LPSCI or LZIC powders were placed in an alumina crucible, with (F)-PDMS placed in another alumina crucible to avoid direct contact. The weight ratio of SEs/(F)-PDMS was 5:1. Subsequent HT was conducted at 243 °C for 1 h. The vacuum

FNFRG

www.advenergymat.de

www.advenergymat.de

SCIENCE NEWS \_\_\_\_\_

**4DVANCED** 

heat-treated LPSCI samples were prepared by HT using a fused silica ampoule sealed under vacuum without (F)-PDMS. NCM  $(\text{LiNi}_{0.90}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2)$  powders coated with Li<sub>2</sub>O-ZrO<sub>2</sub> were used.

Air Stability Characterizations: To investigate the air stability in dry room conditions with dew points of  $-50^{\circ}$ C or  $-10^{\circ}$ C, 150 or 300 mg powder samples (placed on a petri dish) were kept in a custom-made container for a fixed duration. After the exposure, the samples were transferred to an Ar-filled glove box using an airtight desiccator. The dew point was controlled within an acceptable error range of dew point of  $\pm 1^{\circ}$ C by cooling dehumidifier (Figure S25, Supporting Information). The ionic conductivities of the dry air-exposed samples were measured without HT. For the humid-atmosphere-exposure experiments, 150 mg powder samples were exposed to saturated humid Ar generated at 60 °C for 6 h (Figure S26, Supporting Information).

Material Characterizations: For cryo-TEM measurements, the samples were loaded onto a lacey Cu grid. To avoid exposure to air, a double-tilt LN2 atmosphere defend holder (Mel-Build) containing a vacuum transfer function was employed for cryo-TEM. Cryo-TEM images were obtained using a JEM-2100F (JEOL) instrument at an acceleration voltage of 200 kV. The XPS measurements were performed with a monochromatic Al K $\alpha$  source (1486.6 eV) at 12 kV and 6 mA using K-Alpha+ (Thermo Fisher Scientific). The samples were mounted on a sample holder in an Ar-filled glove box and transferred to the XPS instrument without air exposure. Raman spectra were collected with an Ar-ion laser beam at an excitation wavelength of 514.5 nm using a LabRAM Aramis instrument (Horiba Jobin Yvon). For TGA-MS measurements, an STA 409 PC Simultaneous Thermal Analyzer coupled with a QMS 403 C Mass Spectrometer was used. Samples (50 mg) were placed in Al<sub>2</sub>O<sub>3</sub> pans. The samples were loaded within 1 min to minimize air exposure. All measurements were conducted in Ar atmosphere, scanning from 30 °C to 800 °C at a scan rate of 10 °C min<sup>-1</sup>. FTIR spectra were recorded using an ALPHA II FT-IR spectrometer (Bruker) within a range of 4000–400 cm<sup>-1</sup>, 24 scans, and resolution of 4 cm<sup>-1</sup> for each spectrum. Powder XRD patterns were obtained using a Rigaku MiniFlex600 diffractometer with Cu K<sub>a</sub> radiation ( $\lambda = 1.5406$  Å). XRD cells containing hermetically sealed SE samples with a beryllium window were mounted on an XRD diffractometer and measured at 40 kV and 15 mA. GPC was performed using Waters 1515, 2414, and 717 (Waters) equipped with a Waters 2414 refractive index detector. Tetrahydrofuran was used as the eluent.

Electrochemical Characterization: Li+ conductivities were measured using the AC impedance method using Li<sup>+</sup>-blocking Ti|SE|Ti symmetric cells. Cold-pressed pellets were prepared at a pressure of 370 MPa. The thicknesses of LPSCI and LZIC were 600 and 400 µm, respectively. The EIS data were recorded at an amplitude of 10 mV and a frequency range of 10 mHz-7 MHz using VMP3 (Bio-Logic). To prepare NCM electrodes in allsolid-state half-cells, a mixture of NCM, SE, and conductive carbon additives (Super C65) was dry-mixed at a weight ratio of 70:30:3 using a mortar and pestle. Li-In counter electrodes (or reference electrodes), which were partially lithiated indium (nominal composition of Li<sub>0.5</sub>In), were prepared by mixing Li (FMC Lithium Corp.) and In (Aldrich, 99%) powders. All-solidstate cells with a diameter of 13 mm, comprising Ti rods as current collectors and a polyaryletheretherketone (PEEK) mold, were assembled using the following procedure. After the SE layers were formed by pelletizing 150 mg of the LPSCI powder, a counter electrode (Li<sub>0.5</sub>In) was placed on one side of the SE layer. After spreading the as-prepared cathode mixture on the other side of the SE layer, the assemblies were pressed at 370 MPa. Electrode mass loading for the half cells were 7.7  $mg_{NCM}$  cm<sup>-2</sup>.

## **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

## Acknowledgements

This work was supported by Samsung SDI, by the program of Phased Development of Carbon Neutral Technologies through the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (NRF-2022M3J1A1085397), by the technology innovation program (20012216) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea), and by the Battery Research Center of Yonsei University.

## **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.

#### Keywords

air stability, hydrophobic coatings, inorganic solid electrolytes, solid-state batteries, sulfides

Received: May 25, 2023 Revised: August 18, 2023 Published online: October 2, 2023

- [1] D. Larcher, J.-M. Tarascon, Nat. Chem. 2015, 7, 19.
- [2] M. Li, J. Lu, Z. Chen, K. Amine, Adv. Mater. 2018, 30, 1800561.
- [3] J. Janek, W. G. Zeier, Nat. Energy 2016, 1, 16141.
- [4] K. H. Park, Q. Bai, D. H. Kim, D. Y. Oh, Y. Zhu, Y. Mo, Y. S. Jung, Adv. Energy Mater. 2018, 8, 1800035.
- [5] A. Sakuda, A. Hayashi, M. Tatsumisago, Sci. Rep. 2013, 3, 2261.
- [6] H.-J. Deiseroth, S.-T. Kong, H. Eckert, J. Vannahme, C. Reiner, T. Zaiß, M. Schlosser, Angew. Chem., Int. Ed. 2008, 47, 755.
- [7] L. Zhou, N. Minafra, W. G. Zeier, L. F. Nazar, Acc. Chem. Res. 2021, 54, 2717.
- [8] T. Asano, A. Sakai, S. Ouchi, M. Sakaida, A. Miyazaki, S. Hasegawa, *Adv. Mater.* 2018, 30, 1803075.
- [9] H. Kwak, S. Wang, J. Park, Y. Liu, K. T. Kim, Y. Choi, Y. Mo, Y. S. Jung, ACS Energy Lett. 2022, 7, 1776.
- [10] H. Kwak, J.-S. Kim, D. Han, J. S. Kim, J. Park, G. Kwon, S.-M. Bak, U. Heo, C. Park, H.-W. Lee, K.-W. Nam, D.-H. Seo, Y. S. Jung, *Nat. Commun.* **2023**, *14*, 2459.
- [11] Y. Tanaka, K. Ueno, K. Mizuno, K. Takeuchi, T. Asano, A. Sakai, Angew. Chem., Int. Ed. 2023, 62, e202217581.
- [12] Y.-C. Yin, J.-T. Yang, J.-D. Luo, G.-X. Lu, Z. Huang, J.-P. Wang, P. Li, F. Li, Y.-C. Wu, T. Tian, Y.-F. Meng, H.-S. Mo, Y.-H. Song, J.-N. Yang, L.-Z. Feng, T. Ma, W. Wen, K. Gong, L.-J. Wang, H.-X. Ju, Y. Xiao, Z. Li, X. Tao, H.-B. Yao, *Nature* **2023**, *616*, 77.
- [13] H. Muramatsu, A. Hayashi, T. Ohtomo, S. Hama, M. Tatsumisago, Solid State Ionics 2011, 182, 116.
- [14] Y.-T. Chen, M. A. T. Marple, D. H. S. Tan, S.-Y. Ham, B. Sayahpour, W.-K. Li, H. Yang, J. B. Lee, H. J. Hah, E. A. Wu, J.-M. Doux, J. Jang, P. Ridley, A. Cronk, G. Deysher, Z. Chen, Y. S. Meng, *J. Mater. Chem. A* **2022**, *10*, 7155.
- [15] Y. Nikodimos, C.-J. Huang, B. W. Taklu, W.-N. Su, B. J. Hwang, Energy Environ. Sci. 2022, 15, 991.
- [16] X. Li, J. Liang, K. R. Adair, J. Li, W. Li, F. Zhao, Y. Hu, T.-K. Sham, L. Zhang, S. Zhao, S. Lu, H. Huang, R. Li, N. Chen, X. Sun, *Nano Lett.* **2020**, *20*, 4384.
- [17] S. Wang, X. Xu, C. Cui, C. Zeng, J. Liang, J. Fu, R. Zhang, T. Zhai, H. Li, Adv. Funct. Mater. 2022, 32, 2108805.
- [18] Y. Nikodimos, W.-N. Su, B. J. Hwang, Adv. Energy Mater. 2023, 13, 2202854.

#### **ADVANCED** SCIENCE NEWS

www.advancedsciencenews.com

- [19] Y. Zhu, Y. Mo, Angew. Chem., Int. Ed. 2020, 59, 17472.
- [20] X. Li, J. Liang, J. Luo, M. Norouzi Banis, C. Wang, W. Li, S. Deng, C. Yu, F. Zhao, Y. Hu, T.-K. Sham, L. Zhang, S. hao, S. Lu, H. Huang, R. Li, K. R. Adair, X. Sun, *Energy Environ. Sci.* 2019, *12*, 2665.
- [21] J. Schnell, H. Knörzer, A. J. Imbsweiler, G. Reinhart, Energy Technol. 2020, 8, 1901237.
- [22] F. Duffner, N. Kronemeyer, J. Tübke, J. Leker, M. Winter, R. Schmuch, Nat. Energy 2021, 6, 123.
- [23] C. Singer, H.-C. Töpper, T. Kutsch, R. Schuster, R. Koerver, R. Daub, ACS Appl. Mater. Interfaces 2022, 14, 24245.
- [24] P. Lu, D. Wu, L. Chen, H. Li, F. Wu, Electrochem. Energy Rev. 2022, 5, 3.
- [25] R. Chen, Q. Li, X. Yu, L. Chen, H. Li, Chem. Rev. 2020, 120, 6820.
- [26] A. Hayashi, H. Muramatsu, T. Ohtomo, S. Hama, M. Tatsumisago, J. Mater. Chem. A 2013, 1, 6320.
- [27] A. Hayashi, H. Muramatsu, T. Ohtomo, S. Hama, M. Tatsumisago, J. Alloys Compd. 2014, 591, 247.
- [28] T. Ohtomo, A. Hayashi, M. Tatsumisago, K. Kawamoto, J. Mater. Sci. 2013, 48, 4137.
- [29] D. Lee, K.-H. Park, S. Y. Kim, J. Y. Jung, W. Lee, K. Kim, G. Jeong, J.-S. Yu, J. Choi, M.-S. Park, W. Cho, J. Mater. Chem. A 2021, 9, 17311.
- [30] G. Sahu, Z. Lin, J. Li, Z. Liu, N. Dudney, C. Liang, *Energy Environ. Sci.* 2014, 7, 1053.
- [31] H. Kwak, K. H. Park, D. Han, K.-W. Nam, H. Kim, Y. S. Jung, J. Power Sources 2020, 446, 227338.
- [32] K. H. Park, D. Y. Oh, Y. E. Choi, Y. J. Nam, L. Han, J.-Y. Kim, H. Xin, F. Lin, S. M. Oh, Y. S. Jung, *Adv. Mater.* **2016**, *28*, 1874.
- [33] A. Banerjee, K. H. Park, J. W. Heo, Y. J. Nam, C. K. Moon, S. M. Oh, S.-T. Hong, Y. S. Jung, Angew. Chem., Int. Ed. 2016, 55, 9634.
- [34] J. Woo, Y. B. Song, H. Kwak, S. Jun, B. Y. Jang, J. Park, K. T. Kim, C. Park, C. Lee, K.-H. Park, H.-W. Lee, Y. S. Jung, *Adv. Energy Mater.* 2023, 13, 2203292.
- [35] Y. Lee, J. Jeong, H. J. Lee, M. Kim, D. Han, H. Kim, J. M. Yuk, K.-W. Nam, K. Y. Chung, H.-G. Jung, S. Yu, ACS Energy Lett. 2022, 7, 171.
- [36] R. Li, Y. Fan, C. Zhao, A. Hu, B. Zhou, M. He, J. Chen, Z. Yan, Y. Pan, J. Long, Small Methods 2023, 7, 2201177.
- [37] A. Hu, W. Chen, X. Du, Y. Hu, T. Lei, H. Wang, L. Xue, Y. Li, H. Sun, Y. Yan, J. Long, C. Shu, J. Zhu, B. Li, X. Wang, J. Xiong, *Energy Environ. Sci.* 2021, *14*, 4115.
- [38] W. D. Jung, M. Jeon, S. S. Shin, J.-S. Kim, H.-G. Jung, B.-K. Kim, J.-H. Lee, Y.-C. Chung, H. Kim, ACS Omega 2020, 5, 26015.
- [39] G. Liu, J. Shi, M. Zhu, W. Weng, L. Shen, J. Yang, X. Yao, *Energy Storage Mater.* 2021, 38, 249.
- [40] Z. Yu, S.-L. Shang, K. Ahn, D. T. Marty, R. Feng, M. H. Engelhard, Z.-K. Liu, D. Lu, ACS Appl. Mater. Interfaces 2022, 14, 32035.

- [41] X. Yang, X. Gao, M. Jiang, J. Luo, J. Yan, J. Fu, H. Duan, S. Zhao, Y. Tang, R. Yang, R. Li, J. Wang, H. Huang, C. Veer Singh, X. Sun, Angew. Chem., Int. Ed. 2023, 62, e202215680.
- [42] X. Zhang, X. Li, S. Weng, S. Wu, Q. Liu, M. Cao, Y. Li, Z. Wang, L. Zhu, R. Xiao, D. Su, X. Yu, H. Li, L. Chen, Z. Wang, X. Wang, *Energy Environ. Sci.* **2023**, *16*, 1091.
- [43] Y. Jin, Q. He, G. Liu, Z. Gu, M. Wu, T. Sun, Z. Zhang, L. Huang, X. Yao, Adv. Mater. 2023, 35, 2211047.
- [44] Z. D. Hood, A. U. Mane, A. Sundar, S. Tepavcevic, P. Zapol, U. D. Eze, S. P. Adhikari, E. Lee, G. E. Sterbinsky, J. W. Elam, J. G. Connell, *Adv. Mater.* **2023**, *35*, 2300673.
- [45] B. W. Taklu, Y. Nikodimos, H. K. Bezabh, K. Lakshmanan, T. M. Hagos,
  T. A. Nigatu, S. K. Merso, H.-Y. Sung, S.-C. Yang, S.-H. Wu, W.-N. Su,
  B. J. Hwang, *Nano Energy* **2023**, *112*, 108471.
- [46] Q. Wang, G. Sun, Q. Tong, W. Yang, W. Hao, Chem. Eng. J. 2021, 426, 130829.
- [47] M. P. Wolf, G. B. Salieb-Beugelaar, P. Hunziker, Prog. Polym. Sci. 2018, 83, 97.
- [48] J. Yuan, X. Liu, O. Akbulut, J. Hu, S. L. Suib, J. Kong, F. Stellacci, Nat. Nanotechnol. 2008, 3, 332.
- [49] W. Zhang, Y. Hu, J. Ge, H.-L. Jiang, S.-H. Yu, J. Am. Chem. Soc. 2014, 136, 16978.
- [50] S. W. Doo, S. Lee, H. Kim, J. H. Choi, K. T. Lee, ACS Appl. Energy Mater. 2019, 2, 6246.
- [51] H. Zhu, X. Li, Y. Pan, G. Liu, H. Wu, M. Jiang, W. Jin, J. Membr. Sci. 2020, 609, 118225.
- [52] Y.-S. Kim, S. H. Jeon, W. Cho, K. Kim, J. Yu, J. Yi, G. Jeong, K.-H. Park, ACS Appl. Energy Mater. 2022, 5, 15442.
- [53] H. Kwak, D. Han, J. P. Son, J. S. Kim, J. Park, K.-W. Nam, H. Kim, Y. S. Jung, Chem. Eng. J. 2022, 437, 135413.
- [54] K. Lee, S. Kim, J. Park, S. H. Park, A. Coskun, D. S. Jung, W. Cho, J. W. Choi, J. Electrochem. Soc. 2017, 164, A2075.
- [55] D. Y. Oh, Y. J. Nam, K. H. Park, S. H. Jung, S.-J. Cho, Y. K. Kim, Y.-G. Lee, S.-Y. Lee, Y. S. Jung, Adv. Energy Mater. 2015, 5, 1500865.
- [56] D. Y. Oh, Y. J. Nam, K. H. Park, S. H. Jung, K. T. Kim, A. R. Ha, Y. S. Jung, Adv. Energy Mater. 2019, 9, 1802927.
- [57] J. Schnell, T. Günther, T. Knoche, C. Vieider, L. Köhler, A. Just, M. Keller, S. Passerini, G. Reinhart, J. Power Sources 2018, 382, 160.
- [58] Y. Morino, H. Sano, K. Kawamoto, K.-I. Fukui, M. Takeuchi, A. Sakuda, A. Hayashi, *Solid State Ionics* 2023, 392, 116162.
- [59] T. Nakano, T. Kimura, A. Sakuda, M. Tatsumisago, A. Hayashi, J. Phys. Chem. C 2022, 126, 7383.
- [60] S. Wang, Q. Bai, A. M. Nolan, Y. Liu, S. Gong, Q. Sun, Y. Mo, Angew. Chem., Int. Ed. 2019, 58, 8039.
- [61] K. Kim, D. Park, H.-G. Jung, K. Y. Chung, J. H. Shim, B. C. Wood, S. Yu, Chem. Mater. 2021, 33, 3669.

ENERG

#### www.advenergymat.de