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High-molecular-weight ethylene-vinyl acetate binder enables uniform electrode architecture and stable silicon–graphite composite anodes for practical sulfide all-solid-state batteries

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Sulfide-based all-solid-state batteries (ASSBs) are recognized as promising next-generation energy storage systems owing to their high energy density and intrinsic safety. Among various anode candidates for ASSBs, silicon–graphite (Si–Gr) composites offer high specific capacity and favorable cycling stability; however, their large volume changes during cycling lead to interfacial degradation, limiting practical applicability. Herein, we report a scalable wet slurry-processed composite anode composed of Si–Gr active material, sulfide solid electrolyte ($\text{Li}_6\text{PS}_5\text{Cl}$), and highly adhesive ethylene-vinyl acetate (EVA) copolymer binder. By optimizing the vinyl acetate content, the EVA binder provides a balanced combination of elasticity and adhesion, effectively preserving intimate interfacial contact within the anode during prolonged cycling. In addition, using high-molecular-weight EVA markedly suppresses binder migration during high-temperature drying, enabling a homogeneous binder distribution throughout the anode. As a result, a pouch-type ASSB employing Si–Gr composite anode, $\text{Li}_6\text{PS}_5\text{Cl}$ -based sheet electrolyte, and $\text{LiNi}_{0.90}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$ cathode delivers a high initial discharge capacity of $199.6 \text{ mA h g}^{-1}$ (3.0 mA h cm^{-2}) at 0.05C and retains 85.6% of its initial capacity after 100 cycles at 0.2C and 30 °C. These results demonstrate that high-molecular-weight EVA effectively enhances interfacial stability in sulfide-based composite electrodes while enabling scalable manufacturing and robust electrochemical performance under practical operating conditions.

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1. Introduction

Sulfide-based all-solid-state batteries (ASSBs) have attracted considerable attention as next-generation energy storage systems due to their intrinsic safety and high energy density.^{1–6} Achieving higher energy density in ASSBs critically depends on the development of advanced anode materials that can deliver high capacity and stable cycling performance. In this regard, silicon–graphite (Si–Gr) composites have emerged as promising candidates, because silicon offers an exceptionally high theoretical capacity, while graphite provides structural buffering and high electronic conductivity, resulting in improved overall electrode performance.^{7–9} Despite these advantages, the practical implementation of Si–Gr composite anodes in ASSBs remains challenging. Silicon undergoes substantial volume

expansion and contraction during repeated lithiation and delithiation, which leads to the formation of numerous voids and mechanical degradation within the composite anode. These structural instabilities disrupt continuous Li^+ ion and electron transport pathways, thereby increasing internal resistance and accelerating capacity fading during cycling.^{10–12} To address these issues, the incorporation of polymer binders with high flexibility and strong adhesion has been widely explored as an effective strategy to enhance interfacial integrity between the solid electrolyte and Si–Gr active materials. Such binders can accommodate the volumetric changes of silicon, maintain intimate interfacial contact, and facilitate continuous Li^+ transport within the composite anode. Consequently, a variety of polymer binder systems have been investigated to improve the interfacial stability and electrochemical performance of composite electrodes in sulfide-based ASSBs.^{13–19}

For the practical fabrication of composite anodes, the conventional wet-slurry process is attractive owing to its compatibility with existing manufacturing infrastructure and its suitability for large-scale production.^{20,21} Nevertheless, the successful implementation of this process for sulfide-based ASSBs presents several critical challenges. Foremost among

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these is the identification of an appropriate polymer binder that is not only processable in a slurry-based system but also capable of maintaining stable interfacial contact within the composite anode. A major obstacle arises from the limited chemical stability of sulfide solid electrolytes against common organic solvents, which severely constrains solvent selection and complicates binder design.^{22–24} These solvent compatibility issues often lead to interfacial degradation or electrolyte decomposition during electrode processing. Furthermore, high-temperature drying is commonly employed to enhance process throughput and productivity; however, such conditions can induce significant binder migration within the electrode during solvent evaporation.²⁵ Binder migration results in an inhomogeneous distribution of polymer binder across the electrode, thereby deteriorating mechanical cohesion and structural stability. This compositional non-uniformity can generate localized current density hotspots, ultimately triggering interfacial delamination, accelerated degradation, and even short-circuits under prolonged cycling.²⁶

In this work, we report Si-Gr based composite anodes with markedly improved interfacial stability, fabricated *via* a scalable wet-slurry process using an ethylene-vinyl acetate (EVA) copolymer binder. EVA is soluble in low-polarity solvents that are chemically compatible with sulfide solid electrolytes such as $\text{Li}_6\text{PS}_5\text{Cl}$, making it well suited for slurry-based processing of sulfide-based ASSBs. Structurally, the ethylene segments ($-\text{CH}_2-\text{CH}_2-$) impart mechanical flexibility and chemical stability, while the vinyl acetate units ($-\text{OCOCH}_3$) facilitate ion-dipole interactions within the composite anode, thereby enhancing interfacial adhesion and ionic transport. Unlike previous work that focused on phase transition-induced interfacial anchoring in sulfide solid electrolyte membranes,²⁷ this study systematically elucidates the role of EVA as a functional binder in the Si-Gr composite anodes. Specifically, we investigate how the vinyl acetate (VA) content and molecular weight govern electrode integrity, binder migration during high-temperature drying, and the long-term electrochemical stability of pouch-type all-solid-state batteries. By varying the VA content, we identify an EVA copolymer containing 60 wt% vinyl acetate as optimal, exhibiting the best cycling performance among the compositions investigated due to its balanced elastic and adhesive characteristics. Building on this optimization, EVA binders with different molecular weights were further prepared to elucidate the influence of molecular weight on binder migration behavior during high-temperature drying. Notably, high-molecular-weight EVA effectively suppresses binder migration through enhanced polymer chain entanglements, resulting in a homogeneous binder distribution across the composite anode after high-temperature drying. To demonstrate practical applicability, a pouch-type all-solid-state full cell comprising Si-Gr composite anode, $\text{Li}_6\text{PS}_5\text{Cl}$ -based sheet electrolyte (thickness: 49 μm), and $\text{LiNi}_{0.90}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$ (NCM90) cathode was fabricated using the optimized EVA binder. The pouch cell employing high-molecular-weight EVA delivers a high initial discharge capacity of 199.6 mA h g^{-1} at 0.05C with an areal capacity of 3.0 mA h cm^{-2} , and maintains 85.6% of its initial capacity after 100 cycles at 0.2C under practical operating

conditions (30 $^{\circ}\text{C}$, 2.5 MPa). These results establish high-molecular-weight EVA as a promising binder that simultaneously enables scalable manufacturing and stable operation of sulfide-based ASSBs under realistic conditions.

2. Experimental section

2.1. Materials

$\text{Li}_6\text{PS}_5\text{Cl}$ (POSCO JK Solid Solution) solid electrolytes with average particle sizes of 1 and 3 μm were used in this work. The finer powder ($d_{50} = 1 \mu\text{m}$) was employed for the fabrication of composite anodes and composite cathodes, whereas the coarser particles ($d_{50} = 3 \mu\text{m}$) were utilized to prepare solid electrolytes, including both pellets and freestanding sheets. The fine powders were selected to enhance interfacial contact and facilitate Li^+ -ion percolation within the composite electrode while maintaining stable electrode fabrication. Silicon-graphite (Si-Gr) composite was synthesized following a previously reported procedure.^{28,29} Briefly, silicon powder (Hanbyul), graphite flakes (Fritsch), and sucrose (Sigma-Aldrich) were homogeneously dispersed in deionized water and subsequently spray-dried using an Eyela spray dryer operated at 500 rpm with an inlet temperature of 110 $^{\circ}\text{C}$. $\text{LiNi}_{0.90}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$ (NCM90; $d_{50} = 5.0 \mu\text{m}$) was kindly supplied by L&F Co., Ltd. To suppress interfacial side reactions with the sulfide solid electrolyte, the NCM particles were coated with a thin boron-based oxide layer prior to electrode fabrication. Acrylonitrile-butadiene rubber (NBR) and ethylene-vinyl acetate (EVA) copolymer binders were purchased from Kumho Petrochemical and Arlanxeo, respectively, and vacuum-dried before use to eliminate residual moisture. *N*-Butyl butyrate (Alfa Aesar) was selected as the solvent for slurry preparation, and Super C65 (Timcal Co., Ltd) was used as the conductive carbon. Lithium metal foil with a thickness of 200 μm (Honjo Metal) was employed as the reference electrode.

2.2. Preparation of composite electrodes

Composite Si-Gr anodes and NCM90-based composite cathodes were prepared using a wet-slurry coating method. For slurry preparation, polymer binder (NBR or EVA) was first dissolved in *n*-butyl butyrate at a concentration of 5.0 wt% to form homogeneous binder solutions. The anode slurry was then obtained by thoroughly mixing Si-Gr active material, $\text{Li}_6\text{PS}_5\text{Cl}$, and the polymer binder in a weight ratio of 70:30:2. The resulting slurry was coated onto a Ni current collector using a doctor blade and subsequently dried under vacuum at either 50 $^{\circ}\text{C}$ for 24 h or 120 $^{\circ}\text{C}$ for 2 h to remove residual solvent. Similarly, the cathode slurry, composed of NCM90, $\text{Li}_6\text{PS}_5\text{Cl}$, Super C65, and EVA60 binder in a weight ratio of 70:27.5:1.5:1.0, was cast onto a carbon-coated Al foil and vacuum-dried under identical conditions. The areal loadings of active materials in the composite anode and the composite cathode were approximately 3.1 and 15.0 mg cm^{-2} , respectively. The lower anode mass loading reflects the higher specific capacity of the Si-Gr composite and was selected to achieve balanced areal capacities with an N/P ratio of approximately 1.2.

2.3. Molecular weight fractionation of EVA60

The molecular weight fractionation of EVA60 was carried out based on its solubility difference in mixed solvent systems. EVA60 (10 wt%) was first completely dissolved in toluene under continuous magnetic stirring to obtain a homogeneous solution. Heptane was then added dropwise until the solution reached its cloud point, indicating the onset of phase separation. To enhance fractionation selectivity and purity, the turbid mixture was heated to 60 °C until it became fully transparent and subsequently cooled to room temperature. Phase separation was induced by stopping agitation and allowing the solution to stand quiescently at room temperature, resulting in the formation of a polymer-rich precipitated phase and a clear supernatant. The precipitate was collected by decanting the supernatant, washed thoroughly with hexane, and finally dried at 60 °C for 12 h.

2.4. Cell assembly

Solid electrolyte pellets were prepared by cold pressing 150 mg of $\text{Li}_6\text{PS}_5\text{Cl}$ powder under a uniaxial pressure of 105 MPa. A composite Si-Gr anode or a composite NCM90 cathode was subsequently positioned on one side of the pellet and further compacted at 430 MPa. Lithium metal foil was then placed on the opposite side of the pellet, and the resulting stack was consolidated under a stack pressure of 60 MPa to form the solid-state cell. For pouch-cell fabrication, a freestanding solid electrolyte sheet was first prepared by a wet-slurry process using $\text{Li}_6\text{PS}_5\text{Cl}$ and EVA60 in a weight ratio of 97.5 : 2.5. After pressing, the electrolyte sheet exhibited a uniform thickness of approximately 49 μm . The pouch-type all-solid-state cell ($30 \times 40 \text{ mm}^2$) was assembled by sequentially stacking the composite Si-Gr anode, the solid electrolyte sheet, and the composite NCM90 cathode, followed by vacuum sealing in an aluminium-laminate pouch. The N/P capacity ratio of the assembled cell was controlled to be approximately 1.2. The sealed pouch cell was subjected to warm isostatic pressing (WIP; ILSHIN Autoclave) at 450 MPa and 60 °C to ensure intimate interfacial contact between the cell components. For electrochemical evaluation, the pouch cell was finally maintained under a constant stack pressure of 2.5 MPa using pressure jigs during cycling tests.

2.5. Material characterization

^1H NMR spectroscopy was employed to verify the chemical structures of EVA copolymers with different vinyl acetate contents using a VNMRs 600 MHz spectrometer (Varian). The thermal properties of the EVA binders were evaluated by differential scanning calorimetry (DSC; DSC25, TA Instruments) over a temperature range from -50 to 100 °C with heating and cooling rates of 5 °C min^{-1} . *Operando* electrochemical pressure measurements were conducted by installing a pressure sensor (GS-I-210, GS Co., Ltd.) inside the pressurized cell to monitor pressure evolution during cycling. X-ray diffraction (XRD) patterns were recorded using a Bruker D8 ADVANCE diffractometer to analyze the crystalline structures of the materials. The cross-sectional morphologies of the composite

anodes were examined by field-emission scanning electron microscopy (FE-SEM; Regulus8230). The cohesive properties of the composite anodes were assessed using a surface and interfacial cutting analysis system (SAICAS; Daipia Wintes). Molecular weight distributions of EVA60 before and after fractionation were determined by gel permeation chromatography (GPC) using a Nexera GPC system. Spatial distributions of the polymer binder within the composite anodes were analyzed by time-of-flight secondary-ion mass spectrometry (TOF-SIMS; TOF SIMS 5, ION-TOF GmbH). The adhesive strength of the composite anodes was measured using a universal testing machine (QM100SE; QMESYS). Internal void formation within the composite anodes after electrochemical cycling was visualized using high-resolution three-dimensional X-ray microscopy coupled with computed tomography (XRM/CT; Xradia 620 Versa, Carl Zeiss).

2.6. Electrochemical measurements

All galvanostatic cycling tests were conducted at 30 °C using a battery testing system (WBCS 3000, Wonatech), as this temperature closely reflects practical operating conditions. Li/Si-Gr half-cells were initially pre-conditioned at a current density corresponding to 0.05C ($1.0\text{C} = 3.6 \text{ mA cm}^{-2}$) within a voltage window of 0.01–1.5 V, followed by prolonged cycling at 0.2C. Similarly, Li/NCM90 half-cells were subjected to a pre-conditioning step at 0.05C and subsequently cycled at 0.2C ($1.0\text{C} = 3.0 \text{ mA cm}^{-2}$) over a voltage range of 3.0–4.3 V. The ionic conductivity of the solid electrolyte was evaluated from AC impedance measurements using an SUS/solid electrolyte/SUS symmetric cell configuration, recorded with a ZIVE MP1 impedance analyzer. All-solid-state pouch-type cells were first activated by a pre-conditioning cycle at 0.05C ($1.0\text{C} = 3.0 \text{ mA cm}^{-2}$). For subsequent cycling, the cells were charged to 4.3 V at a constant current of 0.2C and then held at constant voltage until the current decayed to 50% of its initial value. Discharge was performed at a constant current of 0.2C down to a cutoff voltage of 2.0 V. Electrochemical impedance spectroscopy (EIS) measurements of the pouch-type cells were conducted over a frequency range from 1 mHz to 1 MHz using the same ZIVE MP1 analyzer to obtain AC impedance spectra.

3. Results and discussion

In designing a polymer binder for composite anodes in ASSBs, it is essential to achieve a balanced combination of strong adhesion and sufficient mechanical flexibility to accommodate the large volume changes of active materials during cycling. In this respect, ethylene-vinyl acetate (EVA) copolymers with vinyl acetate (VA) contents ranging from 40 to 70 wt% were employed as polymer binders when preparing the Si-Gr composite anodes. Fig. S1 presents the chemical structure of EVA, together with the ^1H NMR spectra and DSC thermograms of EVA copolymers with different VA contents. As shown in Fig. S1b, the characteristic resonance peak at 2.00–2.05 ppm, assigned to the methyl protons ($-\text{CH}_3$) of the VA units, progressively increases in intensity with increasing VA content, confirming the

successful compositional control of the EVA copolymers. This compositional variation directly influences the thermal and mechanical properties of the binder. As depicted in Fig. S1c, the glass transition temperature (T_g) of EVA increases monotonically with increasing VA content, which can be attributed to the intrinsically higher T_g and reduced chain mobility associated with the polar vinyl acetate segments. Moreover, EVA60 and EVA70 showed no melting transition, indicating that these copolymers are fully amorphous. These results indicate that increasing the VA content enhances the polarity and interchain interactions of the EVA binder, potentially improving interfacial adhesion within the composite anode, while simultaneously reducing chain flexibility. Therefore, careful optimization of the VA content is required to balance adhesion and elasticity, which is critical for maintaining interfacial integrity and mechanical stability in Si-Gr composite anodes under real operating conditions. All EVA copolymers readily dissolved in *n*-butyl

butyrate, a low-polarity solvent known to be chemically compatible with sulfide solid electrolytes, even at high VA contents (Fig. S2). This excellent solubility enables the preparation of homogeneous slurry without the need for highly polar or reactive solvents that could compromise electrolyte stability. To further verify the chemical compatibility of *n*-butyl butyrate with the sulfide solid electrolyte, X-ray diffraction (XRD) analyses were conducted on $\text{Li}_6\text{PS}_5\text{Cl}$ before and after solvent exposure. As shown in Fig. S3, the characteristic diffraction peaks of $\text{Li}_6\text{PS}_5\text{Cl}$ are well preserved after solvent treatment, indicating that the crystalline structure of the sulfide electrolyte remains intact and that no detectable decomposition or phase transformation occurs during wet-slurry process. Based on these results, composite anodes consisting of Si-Gr active material, $\text{Li}_6\text{PS}_5\text{Cl}$, and EVA binders were successfully fabricated by wet-slurry process. The demonstrated solvent compatibility and structural stability of the sulfide electrolyte

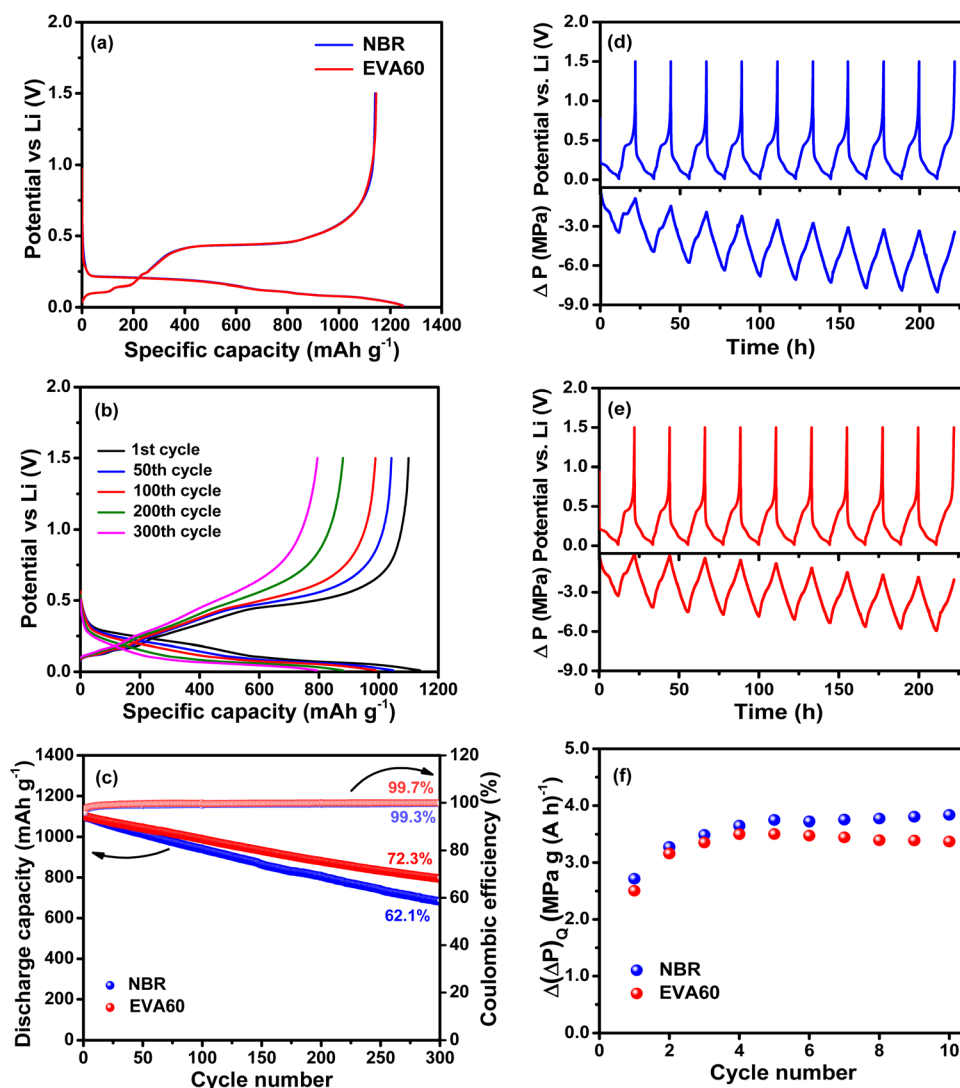


Fig. 1 (a) Voltage profiles of Li/Si-Gr half-cells employing different binders during the pre-conditioning cycle at 0.05C. (b) Charge-discharge curves of the Li/Si-Gr cell with EVA60 and (c) corresponding discharge capacities of Li/Si-Gr cells using different binders at 0.2C and 30 °C. Simultaneous voltage profiles and pressure evolution of Li/Si-Gr cells cycled at 0.2C using (d) NBR and (e) EVA60 binders. (f) Normalized pressure variation of Li/Si-Gr cells as a function of cycling, highlighting the effect of binder type on volume change accommodation.

establish a viable processing window for scalable fabrication of Si-Gr composite anodes for sulfide-based ASSBs. Fig. S4 shows SEM images of the Si-Gr composite anode active materials, where Si particles are uniformly distributed and well embedded within the graphite without agglomeration. This homogeneous microstructure is expected to buffer the volume expansion of Si during lithiation while maintaining continuous electronic pathways through the graphite network. As a result, the Si-Gr composite can achieve improved structural integrity and electrochemical stability during repeated cycling. To determine the optimal EVA composition, the cycling performance of all-solid-state Li/Si-Gr half-cells employing various polymer binders was evaluated. Fig. S5a and b show the voltage profiles during the first pre-conditioning cycle at 0.05C and the discharge capacities upon cycling at 0.2C, respectively. All cells delivered comparable discharge capacities of approximately 1140 mA h g^{-1} in the pre-conditioning cycle. Although similar initial capacities ($1099.0\text{--}1100.3 \text{ mA h g}^{-1}$) were obtained at 0.2C, the EVA60-based cell exhibited the highest capacity retention of 89.8% after 100 cycles. These results demonstrate that EVA60 is the most suitable polymer binder for the composite Si-Gr anode, owing to its optimized balance between adhesion and elasticity.³⁰ EVA60 was compared with nitrile butadiene rubber (NBR), a conventional binder widely used in wet-slurry processing.^{18,31,32} The cycling performance of composite anodes employing these binders was evaluated using Li/Si-Gr half-cells. As shown in Fig. 1a, the NBR-based composite anode delivered a discharge capacity of 1140 mA h g^{-1} during the first pre-conditioning cycle, which is

comparable to that of the EVA60-based anode. Fig. 1b and S6 present the cycling voltage profiles at 0.2C and 30 °C, and the corresponding cycling performance is compared in Fig. 1c. Notably, the EVA60-based cell exhibited superior cycling stability, retaining 72.3% of its initial capacity after 300 cycles and maintaining a higher average coulombic efficiency throughout cycling. This enhanced performance indicates that EVA60 improves interfacial stability, thereby enabling more reversible lithiation and delithiation of the composite anode.³³ Polymer binder should sustain intimate interfacial contact by accommodating the volume changes of active materials and suppressing void formation within the anode during repeated cycling. Accordingly, the ability of the polymer binder to accommodate the volume change of the Si-Gr composite anode was evaluated by monitoring pressure variations during cycling (Fig. S7). Fig. 1d and e show the voltage and pressure responses of Li/Si-Gr half-cells employing NBR and EVA60, respectively, at 0.2C over 10 cycles, while the corresponding normalized pressure variations with respect to the capacity during cycling are compared in Fig. 1f. The EVA60-based cell exhibited a smaller pressure increase after 10 cycles, indicating reduced volume expansion and mitigated void and crack formation originating from the active materials compared with the NBR-based cell.^{28,34} Furthermore, the lower normalized pressure change of the EVA60-based cell suggests that EVA60 more effectively accommodates the volume change of the Si-Gr composite, thereby enhancing the structural integrity of the composite anode during cycling.

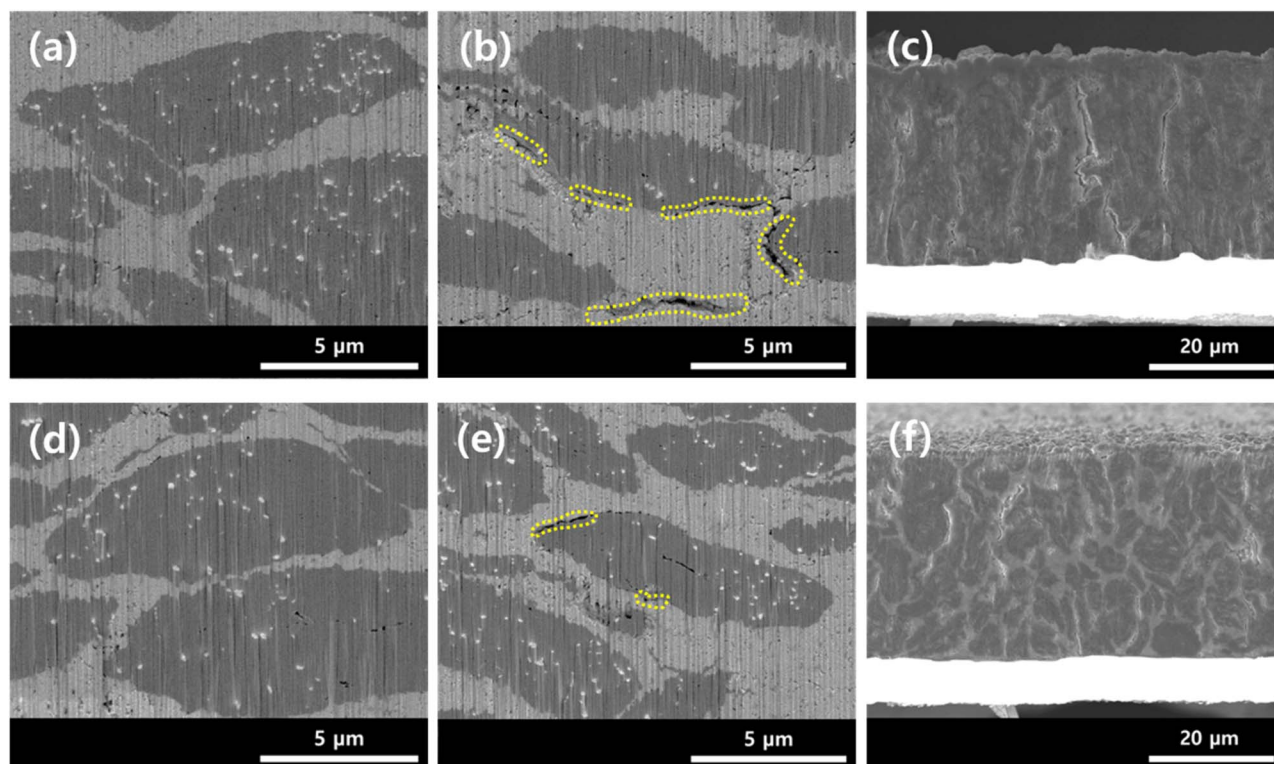


Fig. 2 Cross-sectional SEM images of composite anodes employing different binders: (a–c) NBR and (d–f) EVA60. (a and d) Charged and (b and e) discharged states after the first cycle, and (c and f) charged states after 300 cycles.

Cross-sectional SEM images were examined to elucidate the microstructural evolution of the composite anodes containing different polymer binders during cycling. As shown in Fig. 2a and d, both Si-Gr composite anodes preserved intimate interfacial contact after the initial charging process, irrespective of the binder type. This behavior originates from the volumetric expansion of the Si-Gr active materials upon lithiation, which temporarily compensates for interfacial gaps. Distinct morphological differences emerged, however, after the subsequent discharge. The NBR-based anode exhibited pronounced interfacial gaps between the active material and the solid electrolyte (Fig. 2b), indicating insufficient mechanical accommodation during de-lithiation. In contrast, the EVA60-based anode maintained a more coherent microstructure with substantially fewer cracks and voids (Fig. 2e), demonstrating improved structural integrity. The long-term microstructural stability was further assessed after 300 cycles. As shown in Fig. 2c and f, the charged-state Si-Gr anode employing EVA60 retained continuous internal connectivity, whereas the NBR-based anode suffered from extensive internal disconnections. These

observations confirm that EVA60 more effectively accommodates the repetitive volume changes of the Si-Gr composite, thereby preserving stable interfacial contact with the solid electrolyte. Since the formation of cracks and voids disrupts both Li^+ ion and electron transport pathways, such microstructural degradation accelerates electrochemical performance decay. By suppressing internal disconnection and maintaining robust interfacial integrity, EVA60 directly contributes to the enhanced cycling stability observed for the EVA60-based cells, in good agreement with the cycling results discussed in Fig. 1.

To gain molecular-level insight into the binding behavior of EVA60 within the composite anode, density functional theory (DFT) calculations were conducted, with computational details provided in the SI. As illustrated in Fig. 3a, the acrylonitrile (AN) unit in NBR and the vinyl acetate (VA) unit in EVA were chosen as the representative functional groups responsible for interfacial interactions. For the active-material surface model, the graphite (002) plane – identified as the dominant peak in the XRD patterns of the Si-Gr composite (Fig. S8) – was selected. The calculated binding energies reveal that the VA unit exhibits

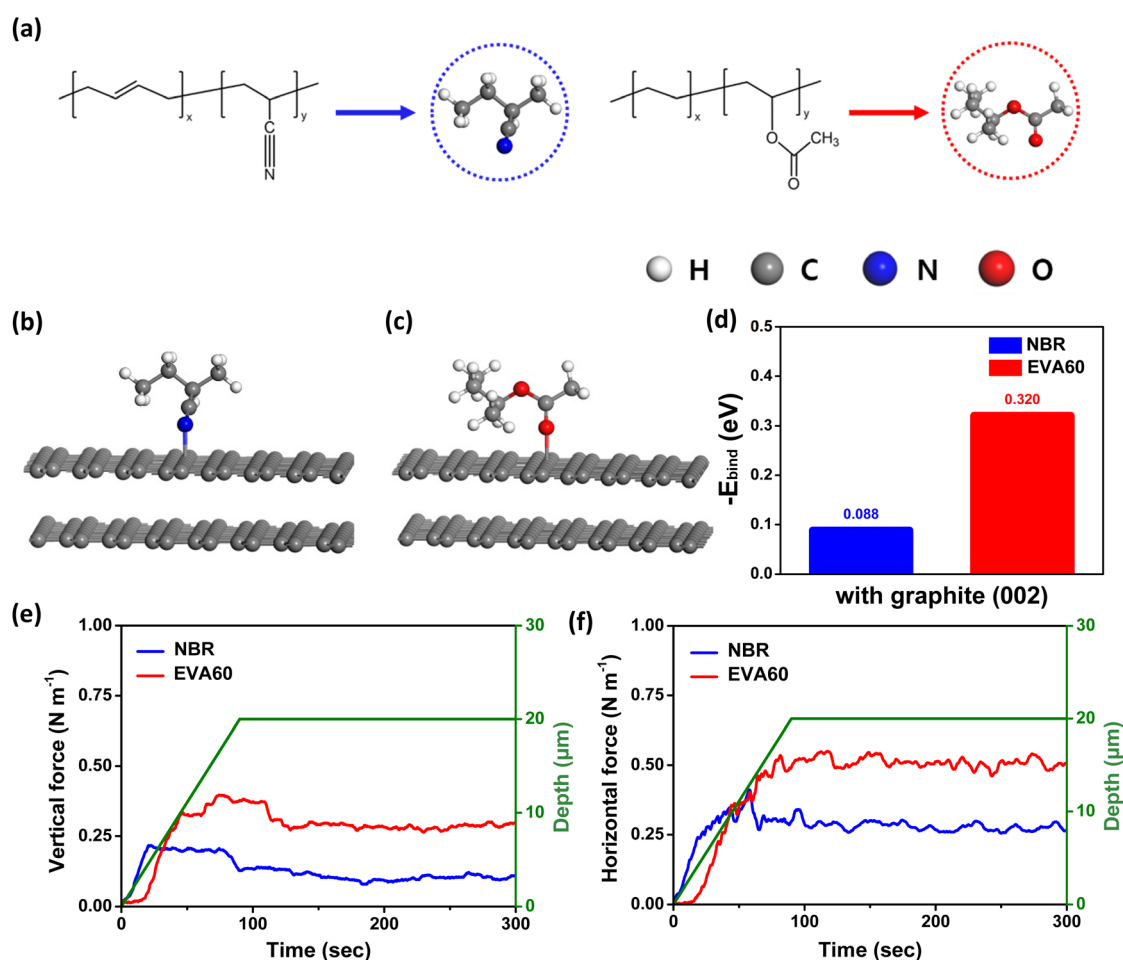


Fig. 3 (a) Molecular structures of acrylonitrile (AN) and vinyl acetate (VA) units representing the polymer binders used for DFT calculations. Most stable binding configurations of (b) AN and (c) VA units on the graphite (002) surface. (d) Calculated binding energies of AN and VA units on the graphite (002) surface. (e) Vertical and (f) horizontal cutting forces measured at the mid-plane of the composite Si-Gr anode during the SAICAS test, reflecting differences in interfacial adhesion and mechanical integrity induced by the type of binder.

a substantially stronger interaction with the graphite surface than the AN unit. Specifically, the binding energies of the AN and VA units with surface carbon were -0.088 and -0.320 eV, respectively (Fig. 3b–d). The stronger binding of the VA unit arises not only from dispersive van der Waals interactions but also from additional polar interactions introduced by the acetate group. In addition to interactions with the active material, the affinity of the polymer units toward the solid electrolyte ($\text{Li}_6\text{PS}_5\text{Cl}$) was evaluated. As shown in Fig. S9, the VA unit exhibits a binding energy toward Li atoms on the $\text{Li}_6\text{PS}_5\text{Cl}$ (100) surface that is approximately 1.6 times higher than that of the AN unit. These results indicate that the VA units in EVA provide stronger interactions with both the Si–Gr active material and the solid electrolyte, thereby promoting more robust interfacial contact within the composite anode. The enhanced binding characteristics of EVA60 were further validated

experimentally using surface and interfacial cutting analysis system (SAICAS) measurements. During the SAICAS test, a cutting blade penetrates the composite anode while the corresponding horizontal and vertical forces are simultaneously recorded. As shown in Fig. 3e and f, the EVA60-based composite anode required higher cutting forces than its NBR-based counterpart, indicating stronger interfacial cohesion. Consistent with these observations, the EVA60-based anode also exhibited higher adhesive strength (Fig. S10). Collectively, these results demonstrate that the VA units in EVA impart superior adhesive and cohesive properties, leading to reinforced interfacial integrity among the Si–Gr active materials, the solid electrolyte, and current collector. This enhanced interfacial robustness plays a crucial role in maintaining the structural stability of the composite anode during repeated electrochemical cycling.

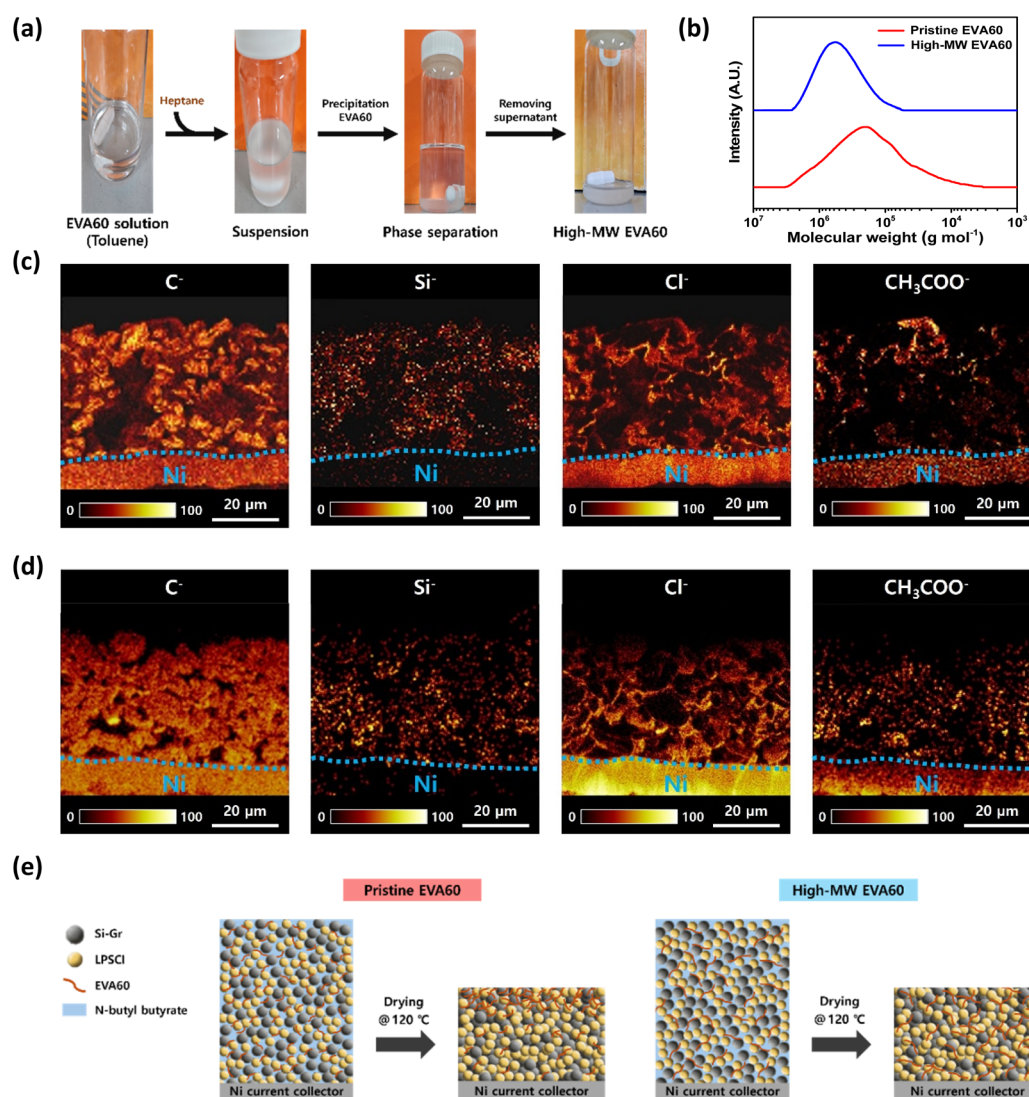


Fig. 4 (a) Molecular weight fractionation process. (b) Molecular weight distributions of pristine EVA60 and fractionated high-MW EVA60 measured by gel permeation chromatography. TOF-SIMS mapping images of C^- , Si^- , Cl^- , and CH_3COO^- species in composite Si–Gr anodes employing (c) pristine EVA60 and (d) high-MW EVA60. (e) Schematic illustration comparing binder distribution within composite Si–Gr anodes employing EVA60 with different MWs.

High-temperature drying of composite anodes is essential for enhancing manufacturing throughput in the battery industry and is therefore a critical requirement for the commercialization of ASSBs. However, drying at elevated temperatures can induce significant binder migration, wherein the binder preferentially accumulates near the electrode surface, leading to compositional inhomogeneity across the electrode thickness.²⁵ In this respect, we investigated the effect of the molecular weight (MW) of EVA60 on binder migration within the composite anode. To this end, EVA60 was fractionated based on the principle that polymers with higher MW exhibit reduced solubility in a given solvent system, as schematically illustrated in Fig. 4a.^{35,36} Specifically, pristine EVA60 (10 wt%) was first completely dissolved in toluene, a good solvent for EVA60. Subsequently, heptane, a nonsolvent for EVA60, was gradually added, inducing the selective precipitation of the high-MW fraction. The precipitated polymer was collected by removing the supernatant containing the low-MW fraction. Hereafter, EVA60 before and after fractionation are referred to as pristine EVA60 and high-MW EVA60, respectively. The molecular weight distributions of pristine EVA60 and high-MW EVA60 were characterized by gel permeation chromatography. As shown in Fig. 4b, the number-average molecular weight (M_n) increased from $8.1 \times 10^4 \text{ g mol}^{-1}$ for pristine EVA60 to $3.9 \times 10^5 \text{ g mol}^{-1}$ after fractionation, confirming the successful isolation of the high-MW EVA60 fraction. To assess the influence of MW on binder migration, composite anodes were fabricated using EVA60 with different MWs and dried at 120 °C for 2 h. The spatial distribution of EVA60 within the anodes was subsequently examined by cross-sectional time-of-flight secondary ion mass spectrometry (TOF-SIMS). Fig. 4c and d present the C^- , Si^- , Cl^- , and CH_3COO^- ion maps of composite anodes prepared with EVA60 of different MWs. The C^- and Si^- signals originate from the Si-Gr composite active materials, while the Cl^- and CH_3COO^- signals are attributed to $\text{Li}_6\text{PS}_5\text{Cl}$ and EVA60, respectively. Regardless of the EVA60 MW, the uniform distributions of the C^- , Si^- , and Cl^- signals across the anode thickness confirm the homogeneous dispersion of the Si-Gr active materials and the solid electrolyte. In contrast, the distribution of EVA60 strongly depended on its MW. The composite anode employing pristine EVA60 exhibited pronounced accumulation of the CH_3COO^- signal near the top surface, indicating severe binder migration during high-temperature drying (Fig. 4c). By comparison, the anode prepared with high-MW EVA60 displayed a uniform CH_3COO^- distribution throughout the entire electrode thickness, as shown in Fig. 4d. These results demonstrate that high-MW EVA60 effectively suppresses binder migration, even under elevated drying temperatures, owing to enhanced polymer chain entanglements that restrict binder mobility, as schematically illustrated in Fig. 4e. This improved binder retention within the composite electrode directly translates into superior interfacial integrity. Consistent with the TOF-SIMS analysis, peeling test results conducted after high-temperature drying further support this result (Fig. S11). The composite anode fabricated with pristine EVA60 exhibited a noticeable reduction in peeling strength, whereas the anode employing high-MW

EVA60 maintained strong adhesion. This enhanced adhesive performance is attributed to the effective suppression of binder migration by the high-MW EVA60. Moreover, SAICAS analysis was performed on composite anodes prepared with pristine EVA60 and high-MW EVA60 (Fig. S12). The cutting force measured at the mid-plane of the high-MW EVA60-based anode was slightly higher than that of the pristine EVA60-based anode. Notably, the high-MW EVA60-based anode exhibited a smoother cutting-force profile with reduced fluctuations, suggesting a more homogeneous internal microstructure resulting from suppressed binder migration during high-temperature drying. These findings demonstrate that the high-MW EVA60 binder effectively suppresses binder migration without compromising the cohesive properties of the composite electrode, while simultaneously promoting more uniform electrode microstructure and stronger adhesion at the electrode/current collector interface.

To validate the practical applicability of EVA60 under realistic operating conditions, an all-solid-state pouch-type Si-Gr/NCM90 full cell was assembled. Beyond its use in the composite anode, the feasibility of EVA60 was systematically evaluated in both solid electrolyte sheets and composite cathodes to assess its versatility as a multifunctional binder. Cross-sectional SEM images of the EVA60-based composite anode and cathode in the as-prepared state are presented in Fig. S13. Both images were acquired at the same magnification to enable a direct comparison of the electrode microstructures. The Si-Gr composite anode exhibits intimate interfacial contact between the active material and the solid electrolyte. Similarly, the composite NCM90 cathode shows a dense and well-connected microstructure, with intimate contact among the active material, solid electrolyte, and conductive additive. These observations indicate that both composite electrodes possess well-integrated microstructures that are favorable for continuous Li^+ -ion transport and stable interfacial contact during electrochemical cycling. The cyclic voltammograms of the $\text{Li}_6\text{PS}_5\text{Cl}$ /EVA60 mixture exhibit no additional redox features compared with pristine $\text{Li}_6\text{PS}_5\text{Cl}$ (Fig. S14), confirming the electrochemical stability of EVA60 within a wide voltage window of 0.01–4.4 V *versus* Li/Li^+ . Solid electrolyte sheet incorporating EVA60 demonstrated excellent mechanical flexibility, with a thickness of 49 μm and an ionic conductivity of 1.42 mS cm^{-1} at 30 °C (Fig. S15). Furthermore, the NCM90-based composite cathode employing EVA60 in the solid-state Li/NCM90 half-cell delivered an initial discharge capacity of $204.7 \text{ mA h g}^{-1}$ corresponding to 3.1 mA h cm^{-2} at 0.05C and maintained 89.4% of its initial capacity after 300 cycles at 0.2C and 30 °C (Fig. S16). Collectively, these findings demonstrate that EVA60 can function as an all-in-one binder for the composite anode, solid electrolyte sheet, and composite cathode, enabling the construction of mechanically robust and electrochemically stable all-solid-state lithium batteries suitable for practical pouch-cell configurations.

Fig. 5a presents the optical image of the all-solid-state pouch type Si-Gr/NCM90 full cell employing EVA60. To evaluate the effect of binder MW under practical conditions, pouch cells fabricated with pristine EVA60 and high-MW EVA60 were cycled

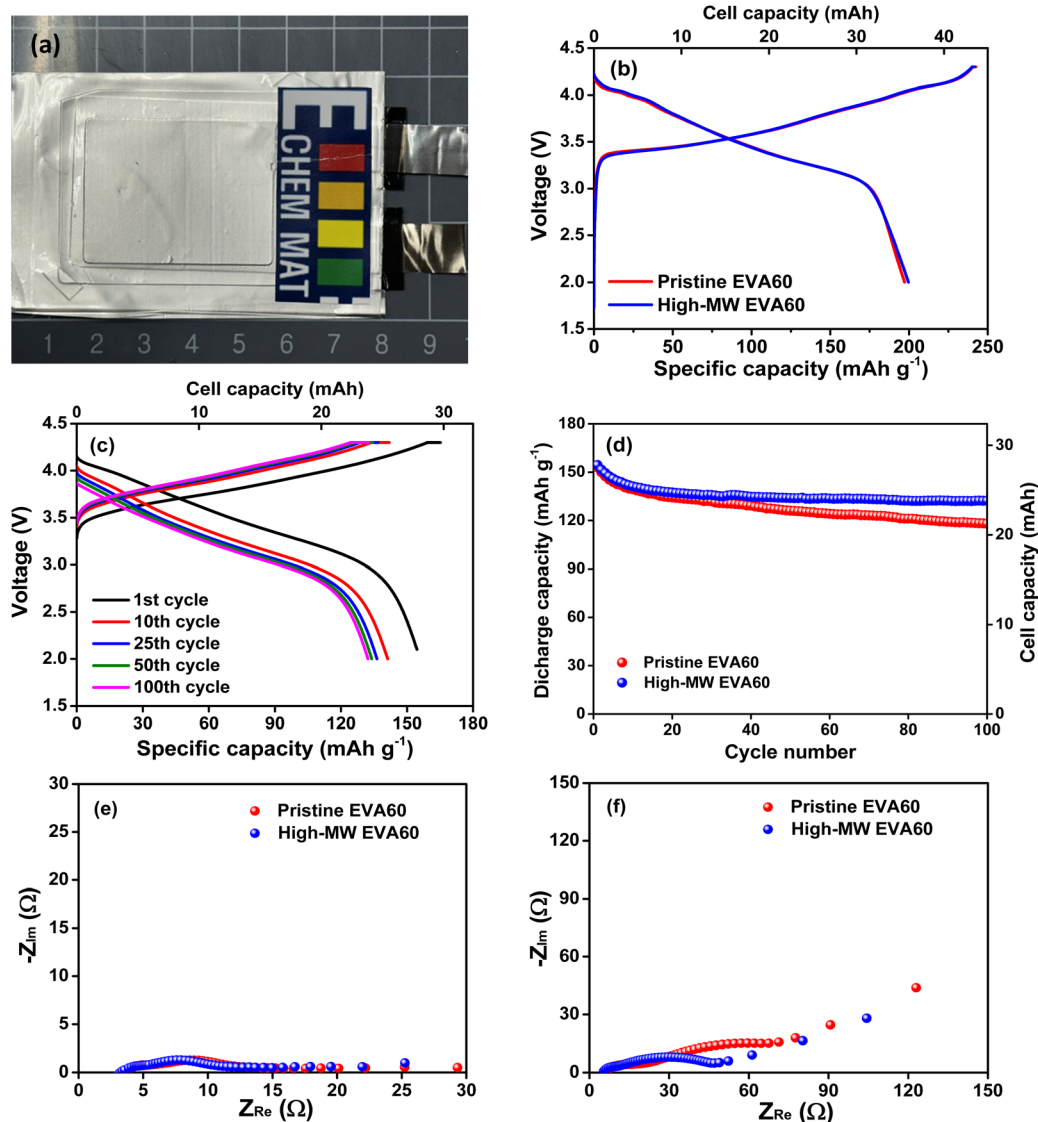


Fig. 5 (a) Photograph of an all-solid-state pouch-type Si-Gr/NCM90 full cell. (b) Voltage profiles of the cells employing EVA60 binders with different molecular weights at 0.05C and 30 °C. (c) Cycling curves of the cell using high-MW EVA60 at 0.2C. (d) Comparative cycling performance of the cells employing EVA60 with different molecular weights at 0.2C and 30 °C. Electrochemical impedance spectra of the cells (e) before cycling and (f) after 100 cycles.

at 30 °C under a low stack pressure of 2.5 MPa. As shown in Fig. 5b, the full cells incorporating pristine EVA60 and high-MW EVA60 delivered initial discharge capacities of 197.2 and 199.6 mA h g⁻¹ at 0.05C, corresponding to cell capacities of 35.5 and 35.9 mA h, respectively. The charge-discharge profiles of the cell employing high-MW EVA60 at 0.2C are presented in Fig. 5c, while the cycling performances of both cells are compared in Fig. 5d. The pouch cell employing high-MW EVA60 exhibited a high initial discharge capacity of 154.5 mA h g⁻¹ and superior capacity retention of 85.6% after 100 cycles. After 200 cycles, the high-MW EVA60-based cell retained 83.2% of its initial capacity, confirming its stable long-term cycling performance (Fig. S17). This enhanced cycling stability is attributed to the strong adhesive characteristics arising from the uniform binder distribution enabled by increased polymer chain

entanglement. A comparison with previously reported all-solid-state full cells (Table S1) demonstrates that the pouch-type Si-Gr/NCM90 cell employing high-MW EVA60 delivers competitive cycling performance under practical operating conditions, including a high areal capacity, low stack pressure, and a pouch-cell configuration. These results highlight the effectiveness of the proposed high-MW EVA60 binder in enabling high-performance, practically relevant all-solid-state batteries. The mechanical robustness and operational reliability of the all-solid-state pouch cells were further examined under abuse conditions. As demonstrated in Fig. S18, the pouch cell continuously powered an LED after nail penetration, cutting, and bending, confirming its excellent mechanical durability, intrinsic safety, and stable operation under severe mechanical stress. AC impedance spectra of the pouch-type full cells were

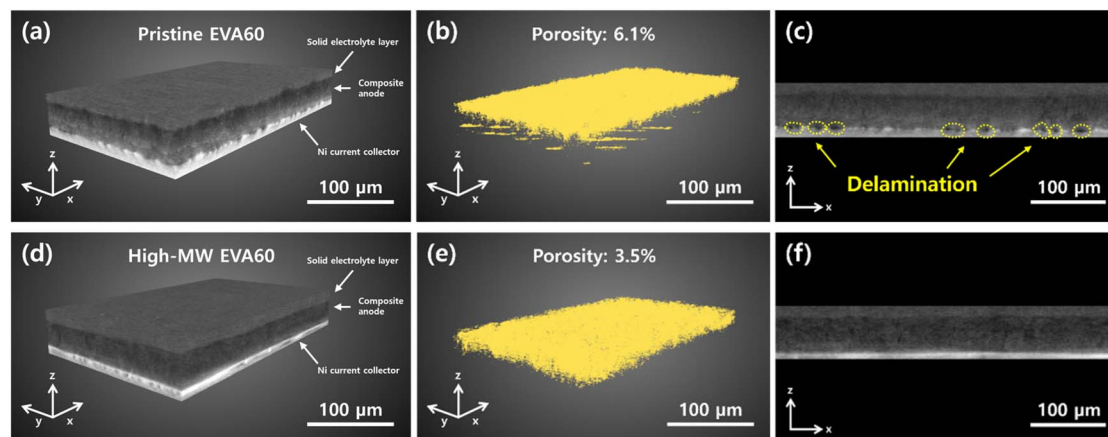


Fig. 6 3D XRM images of composite Si-Gr anodes employing (a and b) pristine EVA60 and (d and e) high-MW EVA60 after 100 cycles in pouch-type full cells. Corresponding 2D transmission images in the xz-plane for composite anodes using (c) pristine EVA60 and (f) high-MW EVA60, enabling direct comparison of internal structural evolution and delamination.

recorded before and after cycling, as shown in Fig. 5e and f. The bulk ionic resistance of the solid electrolyte (R_b) was extracted from the high-frequency intercept on the real axis, while the depressed semicircle was assigned to the interfacial resistance components, including the interphase resistance (R_{hf}) arising from void formation at the interface within the composite electrode, and charge-transfer resistance (R_{ct}), according to the equivalent circuit model shown in Fig. S19.^{37–40} Prior to cycling, both cells exhibited comparable interfacial resistance values, indicating similar initial interfacial conditions. After 100 cycles, however, pronounced differences emerged. The cell employing high-MW EVA60 showed a markedly smaller increase in interfacial resistance, demonstrating the preservation of stable interfacial contact during prolonged cycling. This enhanced interfacial stability is attributed to the strong adhesive and cohesive properties of high-MW EVA60, which effectively suppress interfacial degradation within the pouch-type cell.

X-ray microscopy (XRM) combined with microcomputed tomography (μ -CT) was employed to elucidate the interfacial morphology of the composite anodes after cycling. After 100 cycles, the pouch-type cells were disassembled, and the interfaces between the anode and the current collector were subsequently analyzed. As shown in Fig. 6a and d, high-resolution three-dimensional (3D) reconstructions were obtained from a series of two-dimensional transmission images collected during sample rotation, with internal pores highlighted in yellow (Fig. 6b and e).^{28,41,42} Quantitative analysis reveals that the composite anode employing high-MW EVA60 exhibits a significantly lower internal porosity (3.5%) than that fabricated with pristine EVA60 (6.1%). This reduced porosity indicates that high-MW EVA60 effectively preserves interfacial integrity by accommodating the repeated volume changes of the Si-Gr composite material during cycling. The corresponding two-dimensional transmission images in the xz-plane further corroborate these findings (Fig. 6c and f). The composite Si-Gr anode fabricated with pristine EVA60 displays pronounced contact loss and partial delamination at the interface with the

current collector, which can be attributed to insufficient adhesion resulting from binder migration. In contrast, the composite anode incorporating high-MW EVA60 maintains a smooth and continuous interface without observable delamination. Consequently, the use of high-MW EVA60 enables the retention of stable interfacial contact within the composite anode, even under low stack pressure. Collectively, these structural advantages facilitate scalable electrode fabrication and ensure stable cycling performance of all-solid-state cells under practical operating conditions.

4. Conclusions

In this work, we developed a highly adhesive EVA binder that enables scalable wet-slurry fabrication of Si-Gr composite anodes for sulfide-based ASSBs. By optimizing the vinyl acetate content, EVA60 provides a synergistic balance of elasticity and adhesion, effectively preserving interfacial integrity against the large volume changes of Si during cycling. DFT calculations and mechanical analyses reveal that the vinyl acetate units exhibit strong interactions with both the active materials and the sulfide solid electrolyte, leading to enhanced interfacial stability. Importantly, increasing the molecular weight of EVA60 markedly suppresses binder migration during high-temperature drying by promoting polymer chain entanglement, thereby ensuring homogeneous binder distribution throughout the electrode. As a result, composite anodes employing high-molecular-weight EVA60 exhibit stable interfacial contact within the composite anode and minimized interfacial resistance evolution upon cycling. The versatility of EVA60 further enables its use as an all-in-one binder in composite anodes, solid electrolyte sheets, and composite cathodes without compromising electrochemical stability. A pouch-type ASSB (Si-Gr/ $\text{Li}_6\text{PS}_5\text{Cl}$ -based solid electrolyte sheet/NCM90 cell) operating at 30 °C and 2.5 MPa demonstrates excellent capacity retention and robust mechanical durability under abuse conditions. Collectively, this study establishes high-molecular-

weight EVA as a practical binder platform that simultaneously addresses interfacial stability, process scalability, and reliable cell-level performance, advancing the commercial viability of sulfide-based ASSBs.

Author contributions

Young-Jun Lee contributed to the conceptualization, methodology, data curation, investigation, formal analysis and writing – original draft. Won-Jae Song contributed to the conceptualization, methodology, data curation, investigation and writing – original draft. Jong-Jin Jeon contributed to the conceptualization, investigation and methodology. Jiho Cha contributed to the software, formal analysis and visualization. Kyeong-Weon Park contributed to the formal analysis, validation and investigation. Han-Jo Lee and Gahyeon Im contributed to the validation and investigation. Jongchan Song contributed to the validation, investigation and writing – review and editing. Dong-Won Kim contributed to the conceptualization, supervision, funding acquisition, project administration and writing – review and editing. All authors read and approved the final manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

All the data have been presented in the article or the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d6ta03167f>.

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