

# Unveiling degradation mechanisms of sulfide-based composite cathodes supported by digital-twin modeling: Dry binder versus wet binder

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## ABSTRACT

Sulfide-based all-solid-state lithium batteries (ASSLBs) have garnered considerable attention owing to their high energy density and enhanced safety. In such systems, composite cathodes are commonly fabricated via either a solvent-free dry process or a slurry-based wet process, typically employing polytetrafluoroethylene (PTFE) and acrylonitrile-butadiene rubber (NBR) as binders, respectively. However, a comprehensive understanding of how these binders influence electrochemical performance and degradation mechanisms remains limited. In this study, the effects of PTFE and NBR binders on interfacial degradation are systematically elucidated through electrochemical analyses, morphological characterizations, and digital-twin computational modeling. The results reveal that PTFE effectively mitigates interfacial deterioration by maintaining intimate contact and minimizing void formation, whereas NBR suffers from accelerated interfacial degradation and void growth during prolonged cycling. These findings highlight the critical role of binder-induced interfacial phenomena in determining cell performance and offer valuable insights for optimizing cathode fabrication strategies tailored to each processing route, while guiding the rational design of advanced binders for composite cathodes in ASSLBs.

## 1. Introduction

Over the past decade, the automotive industry has prioritized advancements in rechargeable lithium battery technologies to accelerate the transition from internal combustion engine vehicles to electric vehicle (EV) platforms [1]. For this transition to succeed, the rechargeable lithium batteries must simultaneously deliver enhanced safety and higher energy density [2–4]. During this ongoing transition, lithium-ion batteries (LIBs) employing liquid electrolytes remain the predominant power source for EV applications. However, the inherent limitations of LIBs have become increasingly evident, particularly the flammability of liquid electrolytes and the challenges associated with implementing high mass-loaded cathodes for improving the energy density [5–8]. To address these issues, sulfide-based all-solid-state lithium batteries (ASSLBs) have emerged as promising next-generation energy-storage systems, offering superior safety and high energy density [9–12]. To fully realize the advantages of sulfide-based ASSLBs, optimization of each cell component is essential – particularly the

composite cathode, which critically governs both energy density and cycling stability [13,14]. Among various cathode fabrication methods, two principal approaches have been widely adopted: the solvent-free dry process (hereafter referred to as the “dry process”) and the slurry-casting wet process (hereafter referred to as the “wet process”) [15–18]. These processes differ in the incorporation of solid electrolytes and polymer binders, each offering distinct advantages in interfacial contact and manufacturability. The dry process avoids solvent exposure, thereby preserving the intrinsic ionic conductivity of sulfide-based solid electrolytes [19]. In contrast, the wet process enables the fabrication of uniformly loaded composite cathodes by leveraging the established infrastructure and accumulated expertise of conventional LIB manufacturing [20].

Crucially, the wet process inherently exposes sulfide solid electrolytes, such as  $\text{Li}_6\text{PS}_5\text{Cl}$  (LPSCl), to organic solvents. These electrolytes are highly susceptible to decomposition in polar environments, necessitating the use of non-polar or weakly polar solvents that can simultaneously enhance binder solubility while mitigating side reactions

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between the solvent and cathode components [21]. However, this balance is intrinsically delicate, and it remains unclear which of the two primary factors contributing to cathode performance degradation – solvent-induced decomposition or the binder's intrinsic spatial and chemical behavior – plays the dominant role. To elucidate this issue, polytetrafluoroethylene (PTFE) and acrylonitrile–butadiene rubber (NBR), the representative binders for the dry and wet processes, respectively, were selected as the focus of this study [15,22]. Despite their widespread use, fundamental investigations that clearly differentiate process-induced effects (i.e., solvent exposure) from material-specific effects (e.g., binder structure and distribution) remain limited.

In this study, we systematically investigate the influence of NBR and PTFE binders on the degradation mechanisms of composite cathodes by combining electrochemical measurements, morphological analyses, and digital-twin computational modeling. NBR serves as the representative

binder for wet-processed composite cathodes due to its compatibility with weakly polar solvents and favorable rheological properties [23,24]. In contrast, PTFE is widely employed in dry-processed composite cathodes, owing to its exceptional mechanical robustness and chemical inertness [25,26]. Although both binders have been extensively used in cathode fabrication, a systematic understanding of their respective roles in interfacial degradation remains limited. Here, we aim to clarify whether the degradation of wet-processed cathodes is primarily governed by solvent exposure or by binder-induced structural factors such as deep infiltration and spatial heterogeneity. By coupling experimental characterization with digital-twin modeling, we elucidate the complex interrelations among binder properties, solvent interactions, and cathode integrity. Our results reveal that the PTFE-based dry process enables superior interfacial stability and cycling performance, whereas the NBR-based wet process suffers from accelerated interfacial degradation. This comparative framework provides mechanistic insights into

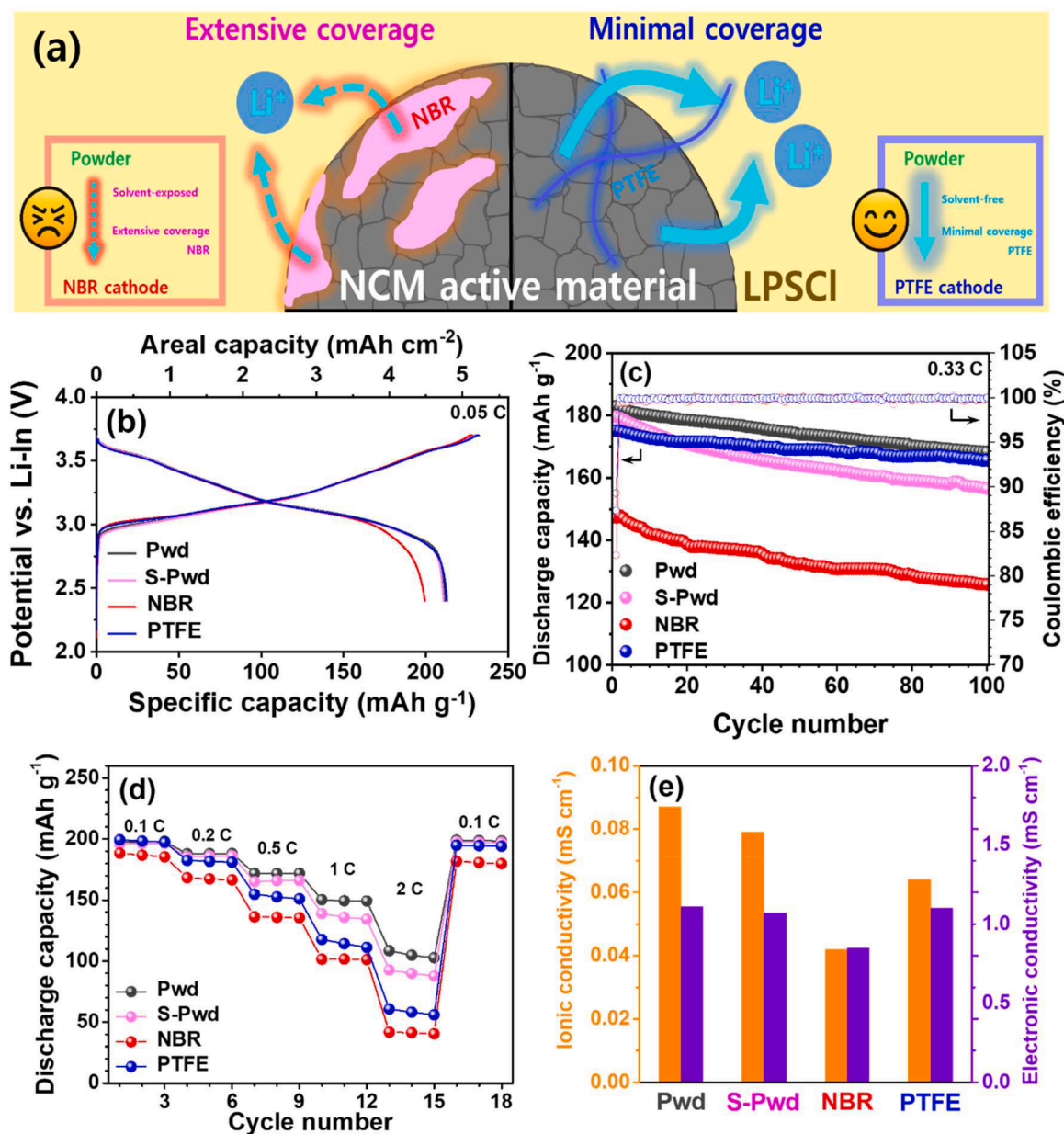


**Fig. 1.** (a) Schematic illustration of binder distribution in composite cathodes: extensive coverage by NBR versus minimal coverage by PTFE. (b) Initial charge and discharge voltage profiles of the cells at 0.05 C. (c) Cycling performance of the cells at 0.33 C. (d) Rate capability of the cells at various C-rates. (e) Ionic and electronic conductivities of composite cathodes employing different binders. All electrochemical tests and conductivity measurements were performed at 30 °C, and the corresponding numerical data are summarized in Table S1.

binder-driven failure pathways and offers valuable guidance for the rational design of next-generation binder systems and cathode fabrication strategies tailored to specific processing environments.

## 2. Results and discussion

To comprehensively elucidate the degradation mechanisms of composite cathodes, it is first necessary to establish a clear understanding of the structural characteristics of wet-processed (hereafter referred to as “NBR”) and dry-processed (hereafter referred to as “PTFE”) cathodes. These two cathode types exhibit distinct morphological features, primarily originating from differences in binder behavior and spatial distribution during fabrication (Fig. 1a). Structurally, the NBR binder does not exhibit a visually distinct morphology but is known to be uniformly dispersed within the composite cathode (Fig. S1a) [23,24]. In contrast, the PTFE binder transforms into a linear fibrillar network under shear forces during the fabrication process, effectively binding the cathode components in dry-processed systems (Fig. S1b) [25,26]. Although both binders possess intrinsically low ionic conductivity compared to the LPSCl solid electrolyte, their distinct spatial distributions result in markedly different electrochemical behaviors. As illustrated in Fig. 1a, the NBR binder permeates deeply into the active material–solid electrolyte interfaces. Conversely, the PTFE binder exhibits a fibrillar morphology confined to relatively narrow interfacial regions within the composite cathode. This contrast in binder distribution suggests that, even at identical binder contents, the presence of non-conductive polymer phases can have fundamentally different impacts on ion transport and interfacial characteristics. Therefore, this structural disparity serves as a critical origin of the distinct electrochemical performance observed in NBR- and PTFE-based composite cathodes. To systematically evaluate how degradation is influenced by both solvent exposure and binder incorporation, four distinct free-standing cathode configurations were prepared, including two reference samples, as illustrated in Fig. S2. The first reference, referred to as the pristine powder (PwD), was prepared without any binder or solvent treatment and consists of a composite mixture of active material, solid electrolyte, and conductive carbon. The second reference, termed the solvent-exposed powder (S-PwD), was produced by exposing the same composite powder to a weakly polar solvent, butyl butyrate, followed by drying without binder addition. These two references serve as essential baselines to independently assess the respective effects of solvent exposure and binder incorporation on cathode degradation. Building on these baselines, the dry-processed cathode was fabricated by mixing the PTFE binder with the pristine composite powder, thereby isolating the effect of binder morphology without solvent interactions. In contrast, the wet-processed cathode was prepared by dispersing the composite powder in butyl butyrate solvent, followed by the addition of the NBR binder [22,27]. Together, these four configurations enable a clear distinction between binder-induced and solvent-induced degradation mechanisms, establishing a robust framework for evaluating how individual fabrication parameters influence the long-term electrochemical stability of composite cathodes. Taking the PwD cell as a baseline, the PTFE-based cell exhibited nearly identical discharge capacity during the initial 0.05 C cycle (Fig. 1b and Table S1). However, at 0.33 C, a noticeable capacity gap emerged, consistent with the expectation that incorporating a non-conductive binder exacerbates capacity loss at higher current rates. Despite this intrinsic limitation, the fiber-like spatial distribution of the PTFE binder minimizes the formation of continuous ion-blocking pathways, thereby mitigating rate-induced capacity fading. Moreover, its interparticle adhesion enhances structural integrity, contributing to improved cycling stability over 100 cycles (PwD: 92.0 %, PTFE: 94.6 % after the 100th cycle) (Fig. 1c, Fig. S3 and Table S1). Nevertheless, the overall rate performance remained inferior to that of the binder-free PwD cell (Fig. 1d). In contrast, the NBR-based cell with bulk coverage binder morphology exhibited pronounced performance deterioration from the outset. At 0.05 C, its discharge capacity

was more than 12 mAh g<sup>-1</sup> lower than that of the PwD cell, and both its initial capacity and capacity retention after 100 cycles at 0.33 C were significantly reduced (PwD: 92.0 %, NBR: 85.4 % at 100th cycle) (Fig. 1c and Table S1). Furthermore, its rate capability lagged behind even that of the PTFE-based cell, indicating that binder morphology and distribution exert a substantial negative influence on ion transport and cycling stability. To decouple the effects of binder incorporation from those of solvent exposure, the S-PwD reference was examined. This binder-free sample, prepared by exposing the pristine powder to butyl butyrate solvent followed by drying, exhibited voltage profiles nearly identical to those of the PwD cell at 0.05 C, with only a slight capacity decrease observed at 0.33 C. Its capacity retention after 100 cycles decreased by approximately 5 % compared to the PwD cell (PwD: 92.0 %, S-PwD: 87.1 %), and the difference in rate capability was minimal (Figs. S3 - S5). The S-PwD exhibits inferior cycling stability but superior rate capability compared to the PTFE-based cathode (Fig. 1c and 1d). The apparent contrast arises from different limiting mechanisms governing rate capability and cycling stability. In the PTFE-based cathode, PTFE binder blocks Li<sup>+</sup> transport pathways more severely than solvent exposure alone, leading to reduced ionic conductivity and inferior rate performance, as supported by ionic conductivity (Fig. 1e). In contrast, the S-PwD cathode maintains better rate capability but suffers from inferior cycling stability due to the absence of a binder that mechanically integrates the electrode components and suppresses interfacial degradation during repeated cycling. These results indicate that solvent exposure alone imposes only a moderate loss, primarily due to a reduction in the ionic conductivity of the solid electrolyte phase within the cathode rather than severe structural degradation. This interpretation is corroborated by XRD analysis, which reveals no significant disruption of the crystal structure (Fig. S6), and by ac impedance measurements showing a moderate decrease in the ionic conductivity of LPSCl (from 1.87 to 0.53 mS cm<sup>-1</sup>) (Fig. S7). Fig. S8 presents the AC impedance spectra of the PwD and S-PwD cells during cycling. The corresponding equivalent circuit used for fitting the impedance data is shown in Fig. S9 [28], where each resistance component (R<sub>bulk</sub>, R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub>) is assigned based on characteristic charge-transport pathways and frequency responses in sulfide-based ASSLBs. Electrochemical impedance spectroscopy (EIS) results after 100 cycles confirmed that the S-PwD exhibited only a slight increase in overall resistance compared to the PwD, with the charge-transfer resistance (R<sub>2</sub>, second semicircle) remaining nearly identical up to the 50th cycle and increasing only modestly thereafter. These findings indicate that the severe performance degradation observed in the NBR cell is primarily governed by the pervasive distribution of its non-conductive binder, rather than by solvent-induced effects, which were shown to exert only a minor influence when decoupled from binder-related factors. The spatially extensive binder distribution in the NBR cell likely impedes Li<sup>+</sup> transport and accelerates performance deterioration, whereas the PTFE-based cell benefits from a spatially confined fiber-like morphology that restricts ion-blocking pathways and preserves structural integrity. Ionic conductivities of the four cathode configurations (Fig. 1e, Fig. S10, and Table S2) support this interpretation [29,30]. The conductivity reduction resulting from the spatial distribution of the NBR binder was substantially greater than that caused by solvent exposure alone. This comparison clearly demonstrates that the primary factor responsible for the performance degradation in the NBR cathode is the presence of the poorly conductive binder, whereas the influence of solvent exposure on LPSCl remains relatively minor under the tested conditions.

To elucidate the microstructural mechanisms by which binder distribution influences electrochemical performance, a three-dimensional structural digital-twin modeling was employed. 3D digital-twin modeling is a computational approach that reconstructs realistic three-dimensional electrode microstructures based on experimentally measured parameters such as particle size, density, porosity, and phase distribution. These virtual electrodes are then used to simulate ionic and electronic transport, electrochemical reactions, and current density

distributions under real operating conditions. This technique enables quantitative correlation between electrode microstructure and electrochemical performance, providing insights that are difficult to obtain from experiments alone [31]. Through 3D digital-twin modeling, a spatially resolved and quantitative analysis is achieved to elucidate how the presence and morphology of non-conductive binders influence the formation, continuity, and percolation of  $\text{Li}^+$  conduction pathways surrounding active material particles, as presented in Fig. 2 [31,32]. By incorporating realistic material compositions and experimentally derived ionic conductivity values into the model (Table S2), the simulations captured not only the geometric configuration of electrode components but also their functional consequences on current density distribution throughout the entire cathode volume. These visualizations reveal how binder type governs the microstructural arrangement and phase connectivity within the composite cathode architecture. Four representative cathode models were constructed by integrating solid electrolytes with carbon-binder domain (CBD), each designed to

reproduce the experimentally observed structural characteristics (Fig. 2a and Fig. S11) [32]. The internal morphology of each model was calibrated using experimentally measured ionic conductivities to ensure consistency between the simulations and the actual electrode performance. In the two-dimensional cross-sectional view of the PTFE-based structure, the binder exhibited a confined, linear morphology that caused negligible interference with the surrounding LPSCI particles near the active material. As a result, the surface coverage of solid electrolyte on active material particles slightly increased from 35 % in the Pwd cell to 36 % in the PTFE cell (Fig. 2b and 2c). Although the overall CBD coverage also increased – from 5 % in the Pwd to 9 % in the PTFE cell – this effect was compensated by improved phase packing and stronger adhesive cohesion, both of which promoted a denser structural organization and more effective ionic contact (Fig. S12) [33]. In contrast, the NBR-based cathode displayed a markedly different microstructural configuration. Due to its permeating morphology, the CBD domain occupied a significantly larger fraction in the electrode volume, leading

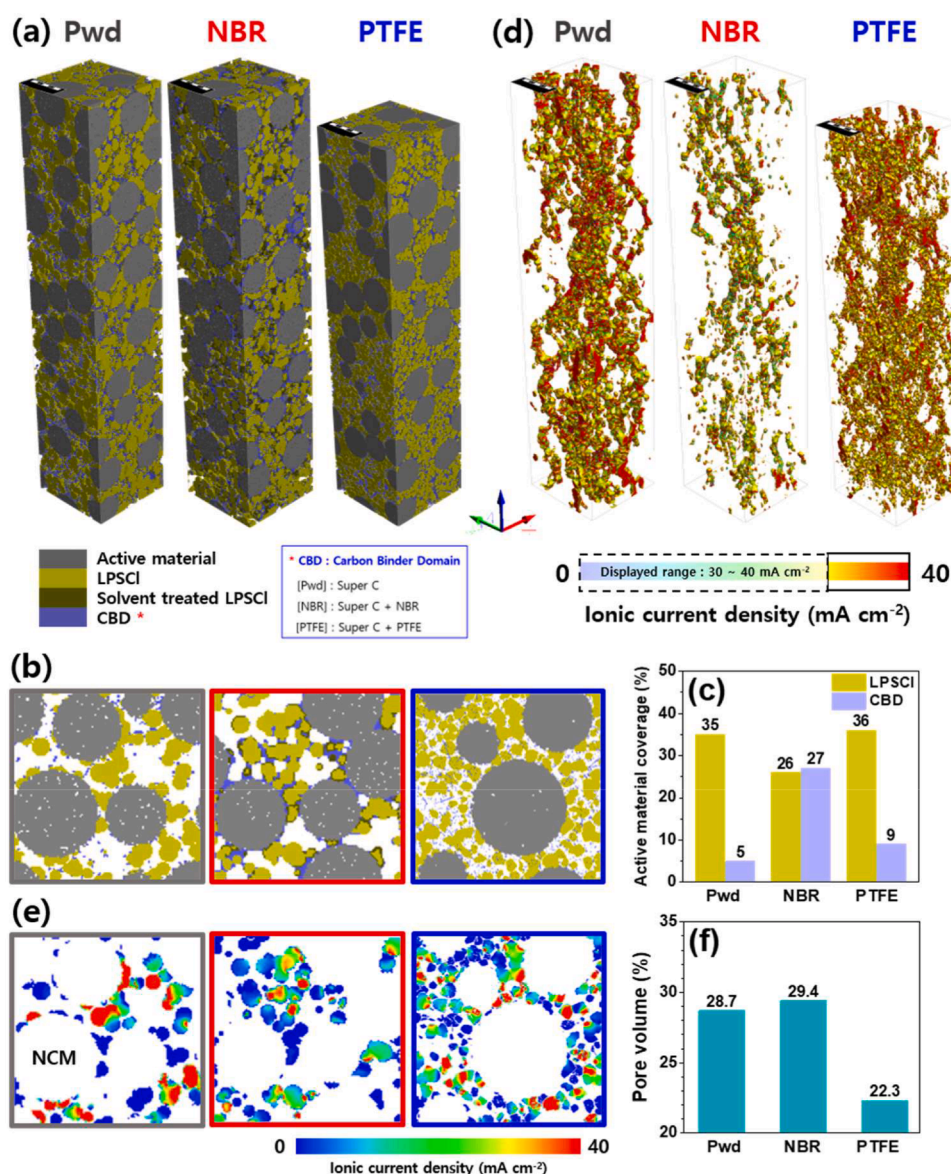


**Fig. 2.** (a) 3D digital-twin structures of composite cathodes modeled with different binders. (b) Corresponding 2D cross-sectional images extracted from the 3D structures, highlighting the spatial distribution of each component's domain within composite cathodes. (c) Composition ratio of LPSCI and CBD surrounding active material. (d) 3D digital-twin structures of composite cathodes modeled with different binders, colored by ionic current density distribution. (e) Corresponding 2D cross-sectional images extracted from the 3D structures, illustrating the local variation in ionic current density. (f) Pore volume ratio in the fabricated composite cathodes.

to substantial disruption of the active material–electrolyte interface. Specifically, the LPSCl coverage decreased from 35 % in the Pwd cell to 26 % in the NBR cell (Fig. 2c), while the CBD interface coverage increased disproportionately. This redistribution effectively displaced both ionically and electronically conductive phases around the active material, resulting in partial insulation of the active surfaces. Notably, the simulated LPSCl coverage trends were in good agreement with experimental results, including those obtained from galvanostatic intermittent titration technique (GITT) measurements (Fig. S13) [34–36]. The spatial configuration of the binder domains also influences the distribution of ionic current density across the composite cathode. The validated modeling results successfully reproduced the general trends observed in electrochemical tests, reinforcing the reliability of the simulated structures (Fig. 2d and Fig. S14a). In the NBR-based model, continuous  $\text{Li}^+$  conduction pathways failed to form under high current density conditions ( $> 30 \text{ mA cm}^{-2}$ ), as shown in both three-dimensional and cross-sectional images (Fig. 2d and 2e). In contrast, the S-Pwd cathode maintained stable high-current regions, indicating that the ionic transport limitations in the NBR cathode originated from binder distribution rather than from chemical degradation of LPSCl (Fig. S14b). In the PTFE-based model, the narrow binder distribution and reduced pore volume arising from the high electrode density facilitated the formation of continuous and robust conduction pathways (Fig. 2f and Fig. S15)

[37]. These findings highlight that the spatial distribution and dimensional morphology of the binder domains critically determine the accessibility of ion and electron transport pathways. While the PTFE system maintains a favorable balance between conductive and non-conductive phases, the NBR system suffers from excessive binder occupation, leading to percolation disruption. Overall, these results underscore the importance of rational binder design not only in terms of content but also spatial localization, in order to minimize electrochemically inactive coverage and maximize active interface exposure.

To further elucidate the degradation mechanisms of NBR- and PTFE-based cathodes beyond their differences in ionic conductivity and spatial coverage, their mechanical binding characteristics were comparatively analyzed (Fig. 3). Two key indicators of long-term stability in composite cathodes are the preservation of ion-conduction pathways and the suppression of interfacial voids, both of which are directly affected by the extent of volume changes during the repeated cycling [38]. To evaluate these aspects, the initial binding behavior of the cathodes was examined under the compacted state of the fabricated ASSLBs. Pressiometry analysis was employed for this purpose, using zero-strain  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  anode active material to ensure that the measured volume change originated solely from the composite cathode, thereby eliminating any influence from anode expansion or contraction (Fig. S16) [17,27,39–41]. During the discharge process of the initial 0.05 C cycle,

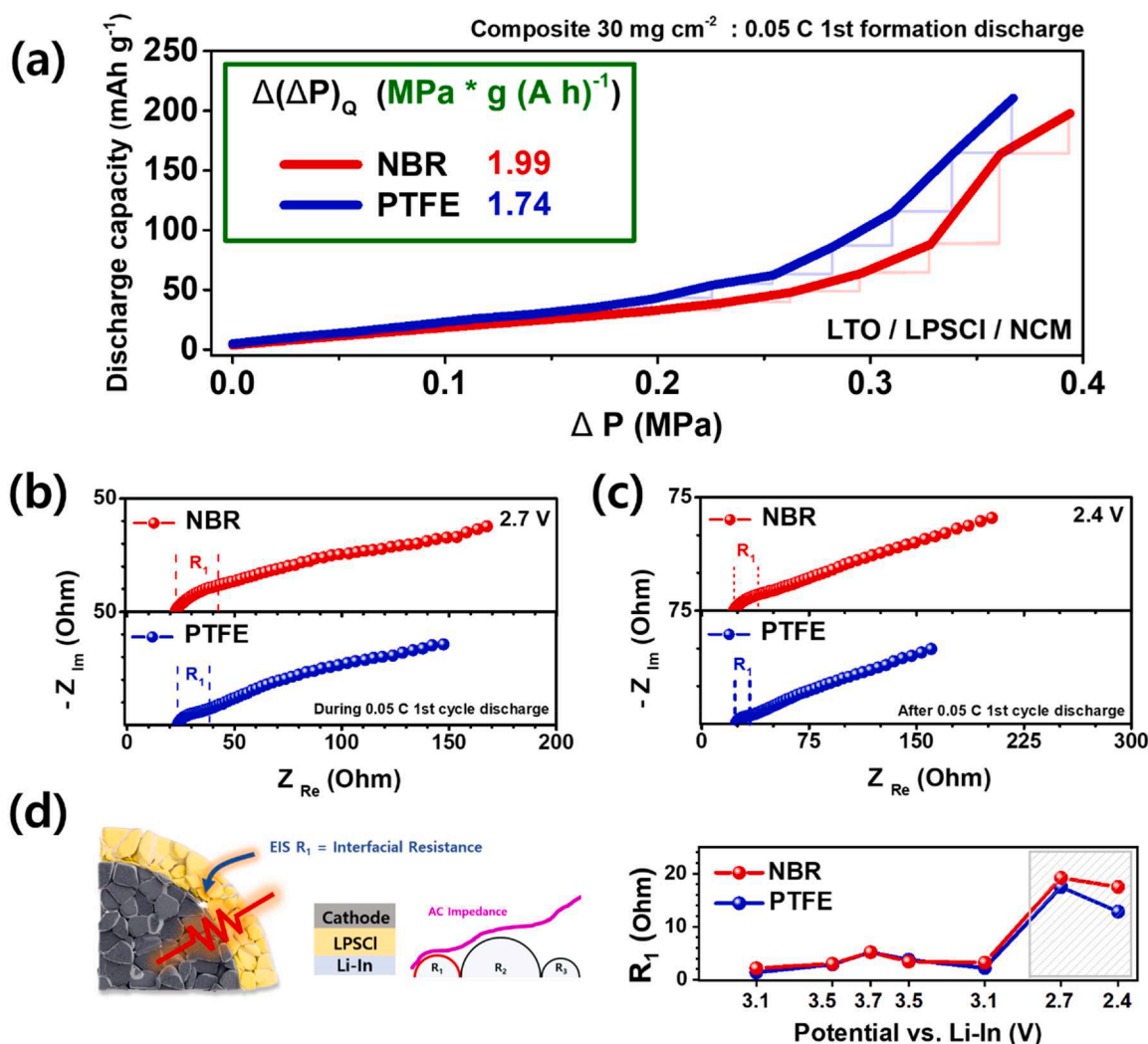


**Fig. 3.** (a) Plot of pressure variation versus discharge capacity during discharge of first formation cycle at 0.05 C. Nyquist plots comparing AC impedance between NBR- and PTFE-based composite cathodes at (b) 2.7 V and (c) 2.4 V. (d) Schematic illustration of interfacial resistance and corresponding resistance values at different cell potential.

the pressure variation per unit capacity was monitored to quantify the extent of volume change (Fig. 3a). The variation ratio was calculated to be 1.99 for the NBR cathode and 1.74 for the PTFE cathode, indicating that the PTFE binder suppressed volume expansion approximately 14 % more effectively. Notably, the PTFE cathode also exhibited about 8 % lower volume change compared with the binder-free Pwd and S-Pwd cathodes, despite showing similar discharge capacities, confirming the intrinsic void-suppressing capability of the PTFE binder (Fig. S17). To further probe the interfacial evolution during  $\text{Li}^+$  extraction and insertion, potential-dependent EIS was performed at selected voltages throughout the initial 0.05 C cycling (Fig. S18a). EIS measurements were conducted after 5-min rest periods at multiple voltage points during charge (3.1, 3.5, 3.7 V) and discharge (3.5, 3.1, 2.7, 2.4 V) to ensure system stabilization (Fig. S18b, Fig. 3b, and 3c). Based on the equivalent circuit shown in Fig. S9, the resistance component  $R_1$  –

representing the interfacial resistance arising from void formation between the active material and the solid electrolyte – was extracted (Fig. 3d and Table S3) [42,43]. Particularly at low voltage states, where discharge-induced expansion becomes significant (as indicated in Fig. 1b for voltages below 3.0 V), distinct differences in  $R_1$  were observed between the two cathodes. At 2.7 V, the NBR cell exhibited an  $R_1$  of 19.2  $\Omega$ , while the PTFE cell showed a slightly lower value of 17.5  $\Omega$ . This disparity became more pronounced at the fully discharged state (2.4 V), where the NBR and PTFE cells exhibited  $R_1$  values of 17.4  $\Omega$  and 12.8  $\Omega$ , respectively. These differences are not attributable to electrochemical byproducts but rather to the intrinsic disparity in binder adhesion, which directly influences void formation at the interface. Importantly, the spatially localized two-dimensional fibrillar network of PTFE enables continuous ion-transport channels and minimizes obstruction around LPSCl, in contrast to the deeply permeating NBR,

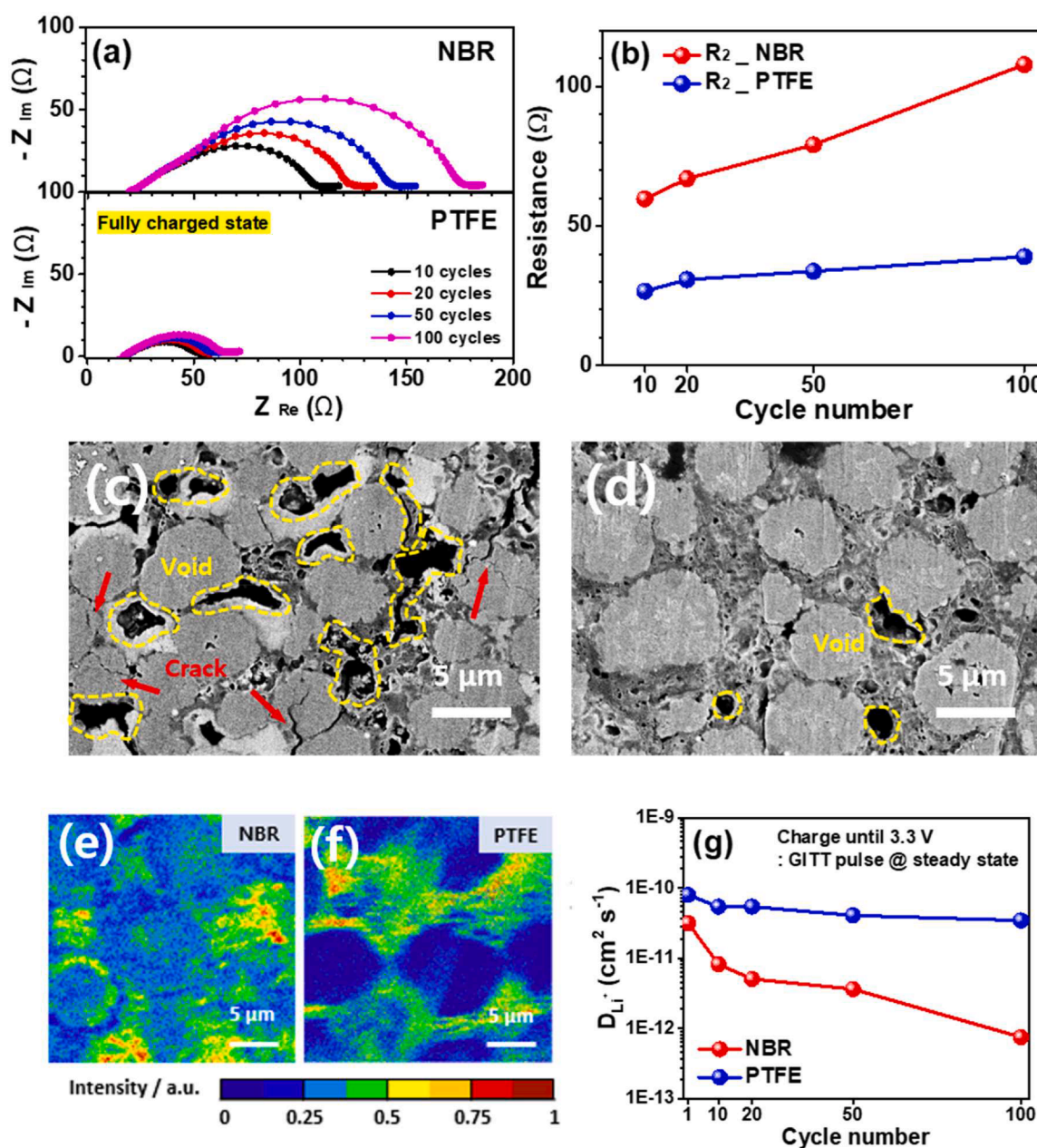


**Fig. 4.** (a) AC impedance spectra of NBR- and PTFE-based cells during 100 cycles at 0.33 C. (b) Corresponding fitted  $R_2$  values in the AC impedance spectra. Cross-sectional SEM images of composite cathodes with (c) NBR and (d) PTFE binders after 100 cycles. ToF-SIMS mapping images showing the  $^7\text{Li}$  distribution on the cross-sectional cathode surface of (e) NBR- and (f) PTFE-based cells, obtained after 100 cycles at the fully charged state. (g) Calculated diffusion coefficients after cycling for NBR- and PTFE-based cells, obtained from GITT pulse application during 0.33 C tests.

which occupies a larger fraction of the active material interfaces and disrupts  $\text{Li}^+$  transport pathways. Surface and interfacial characterization system (SAICAS) measurements were conducted to validate the difference in binding properties between the two cathodes. SAICAS is a mechanical analysis technique that quantitatively measures depth-dependent mechanical properties and interfacial adhesion by precisely cutting and peeling thin layers from a material using a controlled micro-blade. By monitoring the cutting and peeling forces as a function of depth, it provides direct information on interfacial strength and cohesion between layered components [44,45]. As shown in Fig. S19, PTFE-based cathode exhibiting nearly twice the cohesive strength of the NBR-based counterpart. This finding is fully consistent with the observed resistance trends and supports the conclusion that the PTFE-based cathode possesses stronger binding characteristics both in its film state and during the preconditioning cycles. These insights establish a crucial foundation for the subsequent comparative analysis of degradation behavior. Overall, the inferior ionic conductivity of the NBR cathode can be attributed to the extensive permeation of the non-conductive binder, which disrupts the continuity of  $\text{Li}^+$  ion conduction pathways and impedes the formation of direct  $\text{Li}^+$  ion flux. Moreover, its weaker adhesion compared with PTFE makes it more susceptible to interfacial void formation from the earliest stages of cycling. Building on these fundamental findings, the following section investigates how these initial differences evolve into distinct degradation pathways during extended cycling up to 100 cycles.

The capacity fading of the composite cathode during long-term cycling can be primarily attributed to two degradation mechanisms: (1) an increase in interfacial resistance resulting from active material isolation and the formation of side reaction products, and (2) structural degradation of the cathode active material via phase transition into a rock-salt structure. Based on this conceptual framework, EIS measurements were performed at the 10th, 20th, 50th, and 100th cycles during the capacity retention test conducted at 0.33 C (Fig. 4a). As described in Fig. S9,  $R_2$  corresponds to the charge-transfer resistance, and the fitted values are presented in Fig. 4b. In the PTFE-based cathode, the spatially confined, fiber-like binder morphology minimally disrupted  $\text{Li}^+$  ion conduction pathways, resulting in only a negligible increase in  $R_1$  over 100 cycles and a moderate rise in  $R_2$  that eventually reached saturation (Fig. 4b and Fig. S20). In contrast, the NBR-based cathode with its pervasive binder coverage exhibited a continuous increase in both  $R_1$  and  $R_2$  up to the 50th cycle, after which  $R_1$  plateaued while  $R_2$  increased sharply. This divergence suggests that, beyond mid-life, transport limitations within the active material – driven by reduced ionic percolation at the interface – emerge as the dominant degradation mechanism in the NBR system. Cross-sectional SEM images after 100 cycles support this interpretation. That is, the NBR-based cathode exhibits widespread interfacial voids and disrupted solid-electrolyte contact, whereas the PTFE-based cathode maintains a more continuous conduction network (Fig. 4c, 4d and Fig. S21). Consistently, cross-sectional ToF-SIMS mapping of fully charged samples reveals substantial  $\text{Li}^+$  retention within the NBR active material (Fig. 4e and 4f) [46,47]. The ToF-SIMS analysis, conducted on cells at the fully charged state after the 100th cycle, confirms that significant amounts of  $\text{Li}^+$  remain trapped in the NBR cathode. This phenomenon is attributed to severe isolation of the active material caused by excessive interfacial voids, which hinder  $\text{Li}^+$  de-intercalation and result in residual  $\text{Li}^+$  within the active material. In contrast, no discernible  $\text{Li}^+$  signal was detected within the active material of the PTFE cathode, indicating efficient de-intercalation and preservation of interfacial integrity. To investigate the post-50th cycle rise in  $R_2$  observed for the NBR cell (Fig. 4b),  $\text{Li}^+$  diffusion coefficients were determined using the galvanostatic intermittent titration technique (GITT) at selected cycles during the retention test (Fig. 4g, Fig. S22 and Experimental Section in Supporting Information). The diffusion coefficient inherently reflects multiple factors, including the effective contact area between the active material and the surrounding solid electrolyte, as well as the structural integrity of the outermost

layered region in the primary particles. Consequently, it serves as a key indicator for diagnosing cell degradation mechanisms. While the PTFE-based cell exhibited a gradual and steady decrease in diffusion coefficient across all cycles, the NBR-based cell showed an accelerating decline that became markedly pronounced after the 50th cycle. This behavior closely correlates with the sharp increase in  $R_2$  observed in the NBR cell (Fig. 4b), providing strong evidence of the linkage between interfacial degradation and deteriorated ionic transport within the active material.

As shown in Fig. 4, the increase in charge transfer resistance is closely related to the structural degradation of the active material. In particular, the transformation of the surface region of NCM particles from a layered to a rock-salt phase is expected to hinder interfacial reactions and suppress  $\text{Li}^+$  ion transport. To verify this hypothesis and identify the underlying cause of the degradation, a series of XPS and TEM analyses were conducted. First of all, XPS measurements were performed to investigate the oxidative decomposition behavior of LPSCl within the composite cathode (Fig. 5a, 5b, and Fig. S23) [48–50]. At the beginning of electrochemical cycling, phosphate species were detected in both cathodes after the initial cycle, whereas sulfate species – typical products of oxidative decomposition – could not be observed. However, a distinct difference emerged after 100 cycles. Sulfate species were detected in the NBR-based cathode, while the PTFE-based cathode exhibited a similar spectral profile to that observed after the first cycle (Fig. 5c). Furthermore, 3D ToF-SIMS analysis revealed a higher  $\text{SO}^-$  signal intensity in the NBR cathode, providing direct evidence of sulfate species accumulation resulting from LPSCl oxidation (Fig. 5d) [42]. It has been reported that the oxidative decomposition of LPSCl generates byproducts with significantly lower molar volume than pristine LPSCl, thereby promoting the formation of interfacial voids [51]. These sulfate-based byproducts also exhibit higher Young's modulus and brittleness, which can further accelerate void propagation. In this study, the NBR-based cathode exhibited relatively weak interfacial binding strength, leading to the gradual accumulation of voids within the composite cathode during the early stages of cycling (before the 50th cycle). The formation of these voids resulted in anisotropic ion transport pathways around the active material. Such void-induced non-uniform interfacial contact was found to accelerate the oxidative decomposition of the adjacent LPSCl [52]. The resulting decomposition products possess inferior electrochemical and mechanical properties compared to pristine LPSCl, thereby triggering additional cracking and structural degradation near the active material. These damages further deteriorate the surrounding ion transport pathways, leading to a cascade of void accumulation and oxidative decomposition. Consequently, pronounced degradation of the layered structure occurs at the surface of the primary particles. To directly visualize this structural transformation, the active materials were extracted after 100 cycles and analyzed by high-resolution TEM combined with fast Fourier transform (FFT) (Fig. 5e–5j and Fig. S24) [53,54]. In the NBR cathode, the lattice fringes at the particle surface appeared severely disrupted, and FFT analysis revealed distinct diffraction spots corresponding to the rock-salt phase, confirming structural reconstruction in the surface region (Fig. 5f). The rock-salt domains extended approximately 17–22 nm into the primary particles, forming a structurally disordered layer that replaced the original layered stacking. This observation is consistent with previous reports identifying rock-salt reconstruction as a dominant degradation pathway in Ni-rich layered oxides under electrochemical stress [55]. In contrast, the PTFE-based cathode retained comparatively well-ordered lattice fringes, with only a thin reconstructed layer of about 8–10 nm near the surface. FFT analysis further confirmed that residual layered domains remained epitaxially connected to the bulk lattice, suggesting that the layered framework was partially preserved despite surface reconstruction. Such preservation implies that the spatially confined fibrillar distribution of the PTFE binder, in contrast to the deep permeation of NBR, mitigated local strain accumulation and delayed the inward propagation of the phase transformation front.

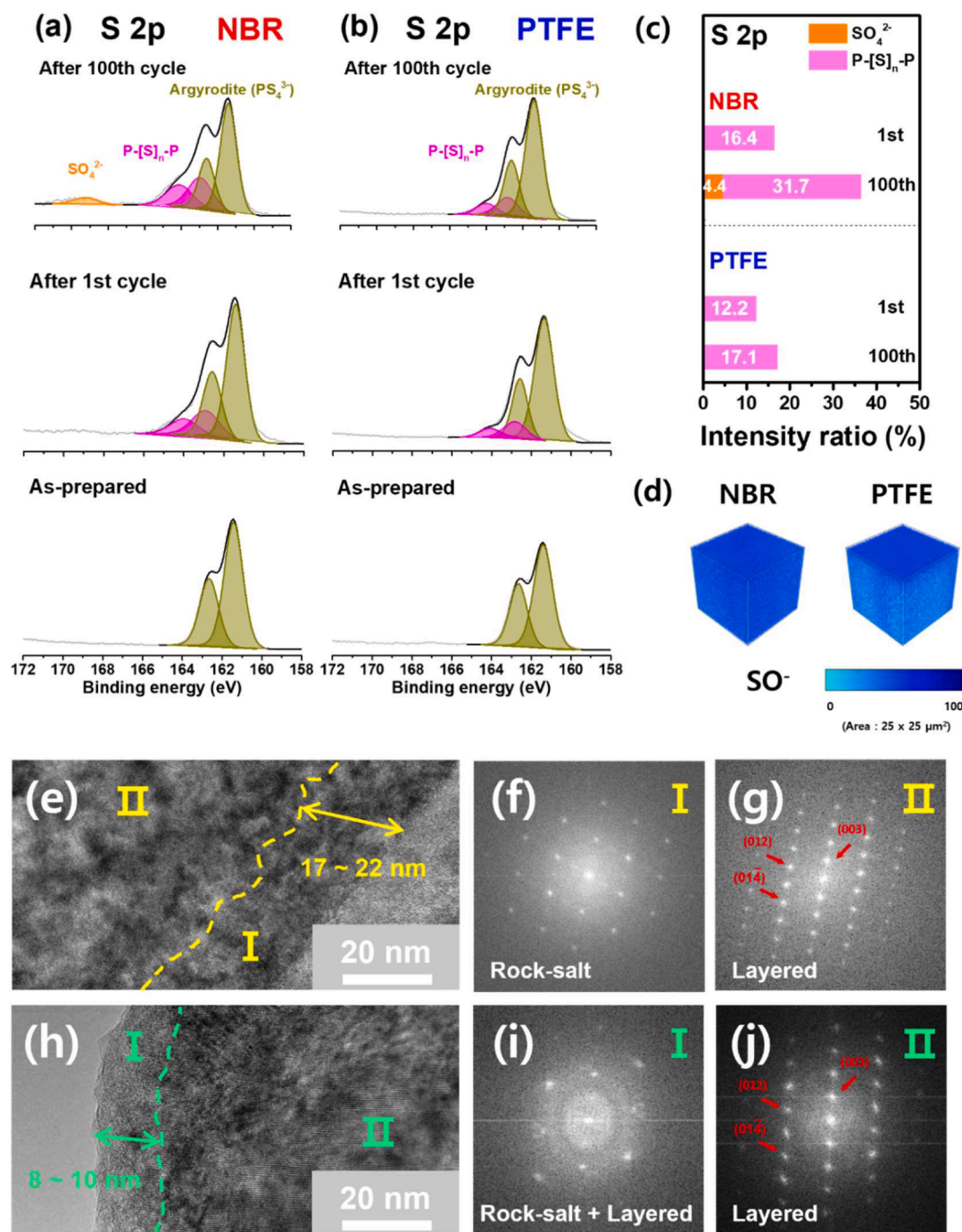


**Fig. 5.** XPS spectra obtained from (a) NBR and (b) PTFE-based cathodes at different cycling stages. (c) Relative area ratio of the fitted S 2p peaks. (d) 3D ToF-SIMS spectroscopy profiles after 100 cycles. TEM images and Fourier-transformed SAED patterns of (e - g) NBR and (h - j) PTFE-based cathodes after 100 cycles.

These findings collectively demonstrate that the spatial distribution and adhesion characteristics of polymer binders play a decisive role in governing the cycling durability of sulfide-based ASSLBs (Fig. 6a). In wet-processed composite cathodes, the NBR binder disrupts continuous ion-conduction pathways and promotes the progressive accumulation of interfacial voids during cycling. These voids accelerate the oxidative decomposition of LPSCl, generating brittle byproducts that further damage the active material surface and trigger a self-accelerating degradation cascade. In contrast, the PTFE binder in dry-processed composite cathodes remains confined within a fibrillar linear network, effectively preserving percolating  $\text{Li}^+$ -ion pathways and suppressing void formation. As a result, the PTFE-based cathode exhibits superior

long-term stability and rate capability. A critical insight from this work is that the detrimental impact of extensive binder occupation in NBR-based cathodes outweighs the relatively minor penalty associated with solvent-induced deterioration of the solid electrolyte. Therefore, the development of wet-process-compatible binders should follow two key design principles: (1) spatial confinement to minimize ion- and electron-blocking effects, and (2) sufficient interfacial adhesion to mitigate void formation during the early stages of cycling. These criteria are consistent with the design strategy of our previously reported distribution-controlled poly(ethylene-co-methyl acrylate-co-glycidyl methacrylate) (EMG) binder system, which exhibited a more confined spatial distribution and stronger interfacial binding than conventional NBR, leading

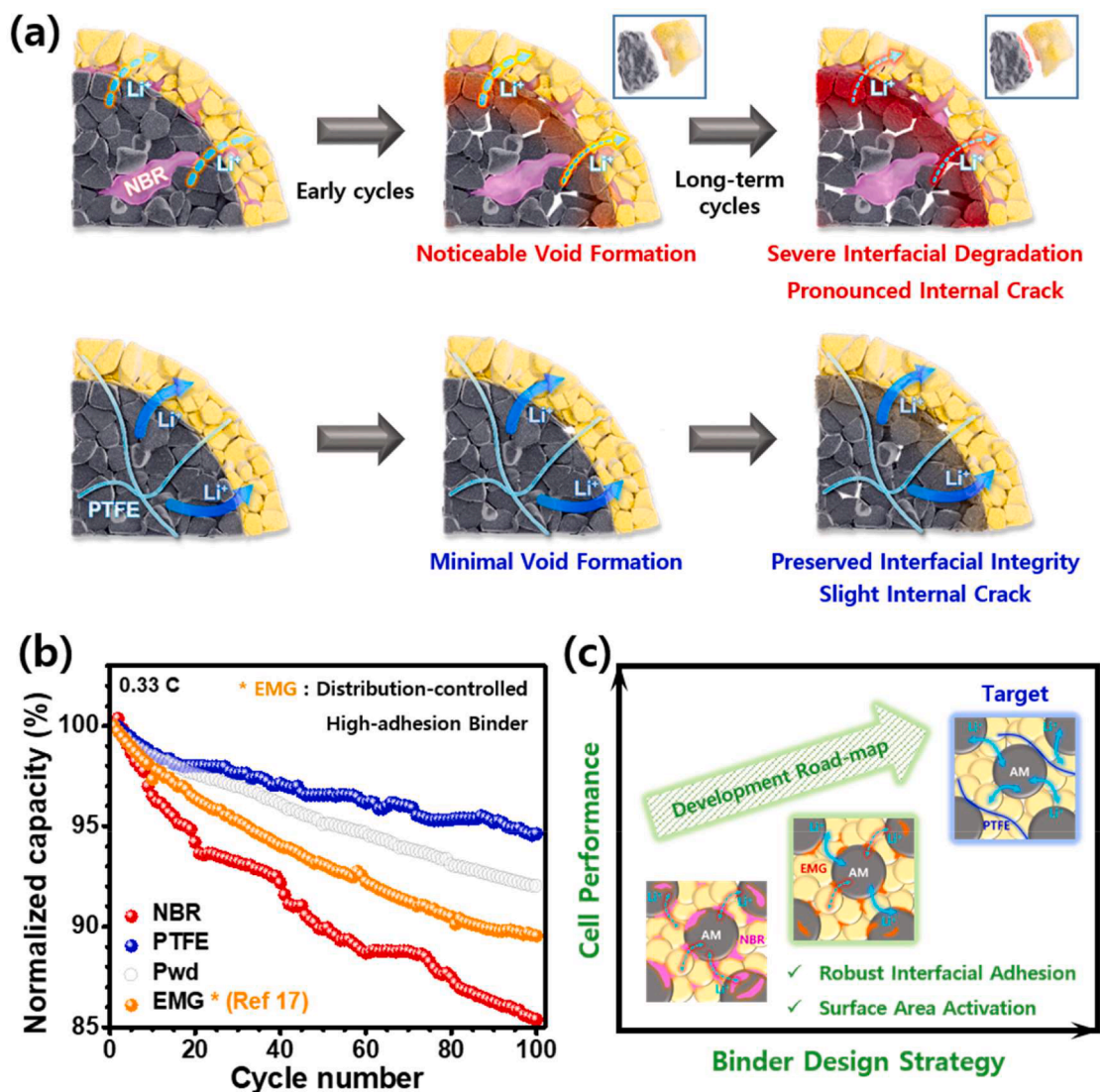


**Fig. 6.** (a) Schematic illustration summarizing the degradation mechanisms in wet- and dry-processed composite cathodes. (b) Electrochemical performance demonstrating the potential improvements achievable through the binder design strategies proposed in this study. (c) Proposed development roadmap for binder design in composite cathodes of sulfide-based ASSLBs.

to enhanced electrochemical performance (Fig. 6b and Fig. S25) [17]. In this context, the binder design strategy illustrated in Fig. 6c – emphasizing strong interfacial adhesion and maximized ionic conduction pathways around the active material – is expected to ultimately enable wet-processed cathodes to achieve electrochemical performance comparable to that of PTFE-based dry cathodes.

### 3. Conclusions

This study systematically elucidates that the morphology, spatial distribution, and interfacial adhesion of polymer binders critically dictate the degradation pathways of sulfide-based composite cathodes in ASSLBs. Integrated electrochemical analyses and digital-twin modeling revealed that the solvent-free dry process, employing PTFE binder, forms a confined two-dimensional fibrillar network that preserves continuous Li<sup>+</sup> ion conduction pathways and structural integrity. In contrast, the slurry-based wet process with NBR binder induces extensive three-dimensional coverage, disrupting ionic percolation and accelerating interfacial void formation and LPSCl oxidation decomposition. This binder-induced structural instability, rather than solvent exposure, was identified as the dominant cause of performance

degradation. Based on these insights, two design principles are proposed for next-generation wet-process-compatible binders: (1) spatial confinement to minimize ion-blocking effects, and (2) strong interfacial adhesion to suppress void propagation. Ultimately, polymer binders should be redefined as active electrochemical components that regulate interfacial stability and structural coherence across solid-solid interfaces. The design roadmap proposed herein highlights binder architectures that balance ionic accessibility with mechanical cohesion, offering a practical framework to bridge the performance gap between wet- and dry-processed sulfide-based ASSLBs.

### 4. Experimental section

#### 4.1. Materials

Two types of Li<sub>6</sub>PS<sub>5</sub>Cl solid electrolytes powder (LPSCl,  $d_{50} = 1$  and  $3 \mu\text{m}$ ) were purchased from Jeong Kwan Co., Ltd. LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> (NCM; L&F Co., Ltd.), Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (LTO; MTI) and Super C (Timcal) were vacuum dried at 100 °C for 12 h prior to use. Polytetrafluoroethylene (PTFE) was purchased from Solvay and acrylonitrile-butadiene rubber (NBR) was supplied from Kumho Petrochemical. Butyl butyrate was

purchased from Sigma-Aldrich. Lithium and indium foils were purchased from Honjo and Nilaco, respectively.

#### 4.2. Electrode preparation and cell assembly

The following procedure was employed to fabricate PTFE-based composite cathodes. First, the cathode components (NCM: LPSCl: Super C: PTFE) were mixed in a weight ratio of 75: 22.5: 1.5: 1. The mixture was blended using a mortar and pestle for 30 min to achieve a uniform distribution. The resulting dough-like mixture was subsequently pressed through a roll-pressing machine (WCRP-1015HG), enabling fibrillation of the PTFE and formation of a cohesive composite cathode sheet. Finally, the resulting sheet type cathode was adjusted to achieve the target mass loading (composite 30 mg cm<sup>-2</sup>). The NBR-based composite cathodes were prepared through the following steps. First, the 5 wt. % of NBR solution was prepared using butyl butyrate solvent. Next, the cathode slurry (NCM: LPSCl: Super C: NBR = 75: 22.5: 1.5: 1 by weight) was cast onto the carbon-coated Al current collector. The cast slurry was dried at 70 °C for 12 h in the heating chamber of glove box. The desired loading was targeted at same with PTFE-based composite cathode sheet. The binder-less powder cathode composite was prepared with a mass ratio of 75: 23.5: 1.5 (NCM: LPSCl: Super C). The mixture was gained through the hand-mixed process for 30 min. When using solvent-exposed solid electrolytes, the LPSCl solid electrolytes were pre-treated with butyl butyrate solvent overnight, followed by drying prior to use. After all of the preparation of electrodes, all-solid-state lithium batteries (ASSLBs) were assembled as follows: First, 150 mg of LPSCl ( $d_{50} = 3 \mu\text{m}$ ) powder was pelletized by pressing at 80 MPa. Next, the prepared three types of cathodes were put on the pellet, and pressed with 350 MPa. And Li-In anode was put on the other side of the pellet, and a Ni foil was attached. Finally, a torque of 30 MPa was pressed. When the LTO composite powder for pressimetry was prepared, the mass ratio of LTO: LPSCl: Super C was fixed to 60: 39: 1. The N/P ratio of pressimetry target cell was set to 1.3. All of the electrode preparation and cell assembly process were performed in the glove box (MBRAUN, O<sub>2</sub> and H<sub>2</sub>O < 0.1 ppm).

#### 4.3. Characterization

The cross-sectional morphology of the composite cathodes was examined by scanning electron microscopy (SEM, Verios G4, FEI). The composite cathode was cut by using a cross-sectional polisher (ArBlade 5000, Hitachi). The time-of-flight secondary-ion mass spectrometry (ToF-SIMS) sample targeted to the cross section was prepared with same method. ToF-SIMS analysis condition had a Bi<sup>1+</sup> ion source; 30 keV and 0.1 pA of current. The ToF-SIMS sample for sputtering 3D analysis was prepared with pristine state, and the analysis condition was set to Bi<sup>3++</sup> ion source; 30 keV and 0.4 pA of current. The cohesive strength of the composite cathodes was measured by using a surface and interfacial cutting analysis system (SAICAS, Daipia Wintes) with a diamond blade. The SAICAS samples were prepared without press (pristine state). X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific) was performed to investigate the decomposition state of the solid electrolytes within composite cathodes. The interface of active material within composite cathodes was investigated using high-resolution transmission electron microscopy (HR-TEM; JEOL 2100F), after the processing with Focused Ion Beam (FIB, Scios, FEI). The selected area electron diffraction (SAED) pattern was analyzed with Gatan Microscopy Suite software (Gatan, Inc.).

#### 4.4. Electrochemical characterization

The cycling performance of the ASSLBs was assessed using a battery cycler (WBS3000, WONA Tech) at 30 °C. At first, two pre-conditioning cycles of 0.05 C (1 C = 4.5 mA cm<sup>-2</sup>) were subjected. It was charged to 3.7 V (vs. Li-In) at a constant current density, and then further charged

at a constant voltage until the current reached 50 % of the charging current. It was then discharged to 2.4 V with 0.05 C. Next, 0.33 C cycle retention test was held with the same routine and cut-off voltage. Ionic conductivity of composite cathodes was evaluated with AC impedance method using (Li/LPSCl/cathode/LPSCl/Li) cell in the frequency range of 10 mHz ~ 1 MHz. Electronic conductivity of composite cathodes was evaluated using (SUS/cathode/SUS) cell. The measurement was conducted using a direct current (DC) method with gradually increased current. The pressimetry measurement result was recorded with pressure sensor and converted using the following equation:

$$\Delta(\Delta P)_Q = \Delta(\Delta P)/Q_{\text{Discharge}}$$

where  $\Delta P$  is the pressure variation during discharge process,  $Q_{\text{Discharge}}$  is a discharge capacity. Potential dependent electrochemical impedance spectroscopy (EIS) was conducted during the first pre-conditioning cycle. The cell was first charged to 3.7 V at a constant current density (0.05 C), during which EIS measurements were performed at 3.1, 3.5, and 3.7 V after 5-min rest at each potential. Subsequently, the cell was discharged to 2.4 V at the same current density, with EIS measurements acquired at 3.5, 3.1, 2.7, and 2.4 V, also following 5-min rest at each corresponding potential. Galvanostatic intermittent titration technique (GITT) measurement during cycle retention test adapted previous basic GITT concept to suit specialized needs [17]. During the cycle retention test, at specific cycles (10, 20, 50, 100th), 1 h rest period was applied after reaching at 3.3 V potential during charge process. Next, a low current (0.05 C) was applied for 1 min, followed by another 1 h rest period. The current application and rest were repeated once more before resuming the regular 0.33 C charge process. To calculate the diffusion coefficient, the following equation can be applied based on this procedure:

$$D = \frac{4}{\pi\tau} \left( \frac{m_{\text{NCM}} V_M}{M_{\text{NCM}} S} \right)^2 \left( \frac{\Delta E_s}{\Delta E_t} \right)^2$$

where  $D$  is the diffusion coefficient of Li<sup>+</sup> in NCM,  $\tau$  is the pulse duration (60 s),  $m_{\text{NCM}}$  is the mass loading (NCM) of the composite cathode,  $V_M$  is the molar volume of NCM,  $M_{\text{NCM}}$  is the molecular weight of NCM,  $S$  is the (effective) active surface area of the active material,  $\Delta E_s$  is the steady-state voltage change, and  $\Delta E_t$  is the transient voltage change.

#### 4.5. Structural digital twin modeling

All of the digital-twin composite cathodes were virtually created via an object-based stochastic generation method using the GrainGeo module in GeoDict2024 while varying the distribution form of binder materials. A convex spherical-shaped NCM (5 g cm<sup>-3</sup>), of which the surface area was controlled to be matched with experimentally measured BET data, was randomly distributed within 3D domain electrode structure with voxel size of 0.2  $\mu\text{m}$ . At next, polyhedron-shaped LPSCl (1.86 g cm<sup>-3</sup>) solid electrolytes and spherical-shaped Super C (1.6 g cm<sup>-3</sup>) were filled in the remaining pore volume. Next, the generated microstructure was discretized into a uniform voxel grid. The ionic current density simulation was performed using ConductoDict module, where the governing transport equations were solved using the Finite Volume Method. Then, a potential difference of 1 V was applied across the top and bottom of the structure. All of the digital twin modeling processes were conducted following the same methodology in our previous study [13,56].

#### CRediT authorship contribution statement

**Seung-Bo Hong:** Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Hyobin Lee:** Investigation, Formal analysis. **Young-Jun Lee:** Methodology, Investigation, Formal analysis, Data curation. **Choyeon Kim:**

Investigation, Data curation. **Yong Min Lee:** Writing – review & editing, Conceptualization. **Un-Hyuck Kim:** Writing – review & editing, Resources, Funding acquisition, Conceptualization. **Dong-Won Kim:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.ensm.2026.104930](https://doi.org/10.1016/j.ensm.2026.104930).

## Data availability

Data will be made available on request.

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