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Invited Review

Review of the electrochemical performance and interfacial issues of high-nickel layered cathodes in inorganic all-solid-state batteries

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Abstract: All-solid-state batteries potentially exhibit high specific energy and high safety, which is one of the development directions for next-generation lithium-ion batteries. The compatibility of all-solid composite electrodes with high-nickel layered cathodes and inorganic solid electrolytes is one of the important problems to be solved. In addition, the interface and mechanical problems of high-nickel layered cathodes and inorganic solid electrolyte composite electrodes have not been thoroughly addressed. In this paper, the possible interface and mechanical problems in the preparation of high-nickel layered cathodes and inorganic solid electrolytes and their interface reaction during charge–discharge and cycling are reviewed. The mechanical contact problems from phenomena to internal causes are also analyzed. Uniform contact between the high-nickel cathode and solid electrolyte in space and the ionic conductivity of the solid electrolyte are the prerequisites for the good performance of a high-nickel layered cathode. The interface reaction and contact loss between the high-nickel layered cathode and solid electrolyte in the composite electrode directly affect the passage of ions and electrons into the active material. The buffer layer constructed on the high-nickel cathode surface can prevent direct contact between the active material and electrolyte and slow down their interface reaction. An appropriate protective layer can also slow down the interface contact loss by reducing the volume change of the high-nickel layered cathode during charge and discharge. Finally, the following recommendations are put forward to realize the development vision of high-nickel layered cathodes: (1) develop electrochemical systems for high-nickel layered cathodes and inorganic solid electrolytes; (2) elucidate the basic science of interface and electrode processes between high-nickel layered cathodes and inorganic solid electrolytes, clarify the mechanisms of the interfacial chemical and electrochemical reactions between the two materials, and address the intrinsic safety issues; (3) strengthen the development of research and engineering technologies and their preparation methods for composite electrodes with high-nickel layered cathodes and solid electrolytes and promote the industrialization of all-solid-state batteries.

Keywords: all-solid-state lithium-ion battery; high-nickel layered cathode; inorganic solid-state electrolyte; cathodes and electrolyte interface

1. Introduction

Owing to their wide usage in all kinds of portable electronic products, lithium-ion batteries have become the mainstream of new energy vehicle power batteries and are expected to achieve large-scale commercial application in the energy storage sector and become one of the key supporting technologies to support carbon neutral and emission peaks in the energy sector [1–2]. As an energy storage device with high specific energy and long life, lithium-ion batteries have been employed in electronic products, electric vehicles, and transoceanic space fields [3–4]. Mainstream lithium-ion batteries use metal oxides for the cathode and graphite, carbon, silicon, and metal oxides for the anode; hence, their operating voltage and energy density are difficult to increase. In ad-

dition, organic liquid electrolytes have a low flash point and poor thermal stability and easily cause fire and even explosion. Therefore, high requirements must be fulfilled to ensure the energy density and safety of lithium-ion batteries [5–7]. For resolution, attention was paid to the development and application of all-solid-state lithium-ion batteries (ASSLBs). ASSLBs use inorganic nonflammable solid-state electrolytes (SSEs) to greatly improve the safety performance of lithium-ion batteries; the hard solid–solid interface can also be directly matched to the lithium metal cathode to further enhance the energy density of the battery [8–9].

Inorganic SSEs are mainly classified as sulfides, oxides, halides, and others such as nitrides, $\text{Li}_2\text{PO}_2\text{N}$ (LIPON), hydrides, and peroxides. According to morphology, sulfide SSEs are mainly categorized as glassy (Li_2S – P_2S_5 , Li_2S –

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GeS₂, and Li₂S–SiS₂) [10–11] or crystalline (Li₁₀GeP₂S₁₂ system and its derivatives and Li₆PS₅X (X = Cl, Br, I) and its derivatives) [12–13]. Lithium sulfide SSEs have high lithium-ion conductivity at room temperature, but their narrow electrochemical window and poor cathode/electrolyte interfacial phase solubility limit their use in ASSLBs. Most oxide SSEs are in a crystalline state, including garnet-type Li₇La₃ZrO₁₂ (LLZO), chalcogenide-type La_{2/3-x}Li_{3x}TiO₃, NASICON-type Li_{1+x}Al_xGe_{2-x}(PO₄)₃, and Li_{1+x}Al_xTi_{2-x}(PO₄)₃ (LATP); their further applications are affected by some factors, such as high air and thermal stability, large interfacial impedance between crystals, and difficult preparation as an electrode/electrolyte [14]. Halide SSEs exist mainly in a crystalline form and have a general chemical formula Li_aMX_b, with M being a metallic element (M = Sc, Y, M, Al, In) or a nonmetallic element, such as N, O, and S (X = F, Cl, Br, I). Halide SSEs present several advantages over other types of solid electrolytes in terms of wide electrochemical windows, no side reaction with oxide cathode materials, good air stability, and scalability [15–16]. The development of SSEs has also substantially contributed to the advancement of ASSLBs, and the compatibility between cathode materials and ASSLBs has become one of the main research goals. Early research primarily focused on matching LiFePO₄ and LiCoO₂ with SSEs. With improvements in the lithium-ion conductivity and chemical stability of SSEs, studies have gradually shifted to matching cathode materials with high voltage and high specific capacity to achieve high energy density [17–19]. High-nickel layered cathodes, with general formulations of LiNi_xMn_yCo_{1-x-y}O₂ (NMC) and LiNi_xCo_yAl_{1-x-y}O₂ (NCA, $x \geq 0.6$), have the advantage of achieving high operating voltage and high volumetric specific energy but the disadvantage of introducing safety hazards in the liquid system that restrict their further application [20–22]. High-nickel layered cathodes are matched with inorganic SSEs into ASSLBs to theoretically achieve high specific energy and high safety [8]. Recent studies revealed the good potential of electrochemical systems with high-nickel layered cathodes and solid electrolytes. Li *et al.* and Deng *et al.* [23–26] studied the application of halide SSEs and SSEs in an electrochemical system with high-nickel layered cathodes and solved the technical problem of Li₃InCl₆ with low cost and easily scalable preparation.

Owing to the high specific energy characteristics of lithium-ion batteries with high-nickel layered cathodes and the urgent safety problems, ASSLBs, especially those with inorganic SSEs, have become the future development trend [27]. Considering the lack of related reviews, this article studies the electrochemical systems of high-nickel layered cathodes and inorganic SSEs. Research progress in the use of high-nickel layered cathodes in inorganic SSEs, interface problems, and coatings of high-nickel layered cathodes is compared between domestic and international works in the past five years. The future development trend is foreseen, and the research directions that need to be further strengthened are proposed.

2. Electrochemical performance of high-nickel layered cathodes in inorganic ASSLBs

Fig. 1 shows the initial cycle curves and differential capacity analysis (dQ/dV) curves of high-nickel layered cathodes in inorganic SSEs and liquid electrolytes [28–29]. The Ni content (x) of LiNi_xCo_yMn₂O₂, a high-nickel layered cathode, ranges from 0.6 to 0.9; LiNi_xCo_yAl₂O₂ is also included. The inorganic SSE used is oxide, sulfide, and halide. The figure reveals that the high-nickel layered cathodes exhibit similar electrochemical properties in inorganic SSEs and liquid electrolytes and undergo phase changes such as H1–H2, H2–M, and H2–H3 during the first charge and discharge.

Table 1 lists the electrochemical performance of high-nickel layered cathodes in inorganic SSEs under various conditions. The high-nickel layered cathodes have relatively good electrochemical performance in inorganic SSEs at low current densities; however, their discharge specific capacity still varies from 130 to 200 mAh·g⁻¹ at 0.1 C current density. At high current densities, the capacity of high-nickel layered cathodes in different SSE systems greatly varies due to the influence of SSE material (lithium-ion conductivity and electrochemical and chemical stability), the high-nickel layered cathode itself, and the interface between the high-nickel layered cathode and SSE. External factors also influence the performance of ASSLBs. Different preparation methods for composite electrodes, such as ratio change of active material to the electrolyte, pressure change, and adoption of different mixing methods, affect the capacity of high-nickel layered cathodes in SSEs. This section presents the analysis of how the morphology of the high-nickel layered cathode, the assembly method of high-nickel and SSE composite electrodes, and the preparation parameters in the composite electrodes affect the electrochemical performance of solid-state batteries.

2.1. Comparison of electrochemical performance between polycrystalline and single-crystal high-nickel layered cathodes in inorganic ASSLBs

Structural integrity during the cycling of high-nickel layered cathodes is an important factor in composite electrodes due to its influence on the cycling and rate performance of ASSLBs [38]. High-nickel layered cathodes exhibit two forms of particles: polycrystalline and single crystal. Polycrystalline particles are secondary particles formed by the aggregation of multiple single-crystal primary particles. Owing to the volume variation caused by the phase change in the charging and discharging of high-nickel layered cathodes, the particles crack, fracture, or even rupture; this phenomenon affects the predictability and is advantageous for the formation of polycrystalline high-nickel layered cathodes [17]. Particle cracks and fragmentation can also be found in liquid cells, but the electrolyte can penetrate the cracks and crevices. Different from those in liquid batteries, the active material and electrolyte in solid-state batteries are in solid–solid contact. Internal gaps and cracks are created when

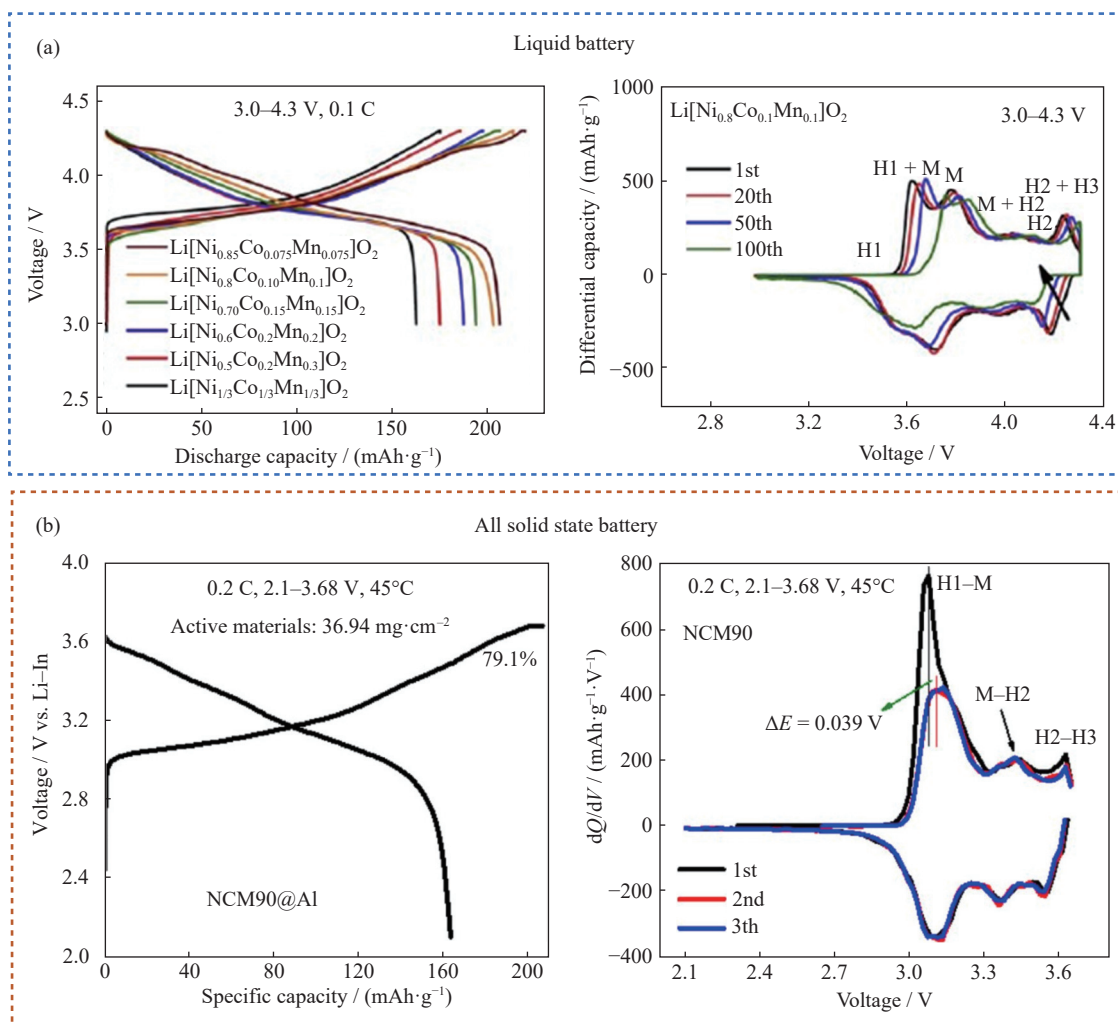


Fig. 1. (a) Initial charge/discharge curves and dQ/dV curves of $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_z]\text{O}_2$ ($x = 1/3, 0.5, 0.6, 0.7, 0.8, \text{ and } 0.85$) liquid battery (0.1 C in 3.0–4.3 V). (b) Initial charge/discharge curves and dQ/dV curves of NCM90 cathodes at 0.2 C, 2.1–3.68 V vs. Li^+/In for sulfide-based ASSLBs. ΔE represents electric potential difference. (a) Reprinted from *J. Power Sources*, 233, H.J. Noh, S. Youn, C.S. Yoon, and Y.K. Sun, Comparison of the structural and electrochemical properties of layered $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_z]\text{O}_2$ ($x = 1/3, 0.5, 0.6, 0.7, 0.8 \text{ and } 0.85$) cathode material for lithium-ion batteries, 121–130, Copyright 2013, with permission from Elsevier; (b) reprinted from *Electrochim. Acta*, 391, X.L. Li, Y.M. Sun, Z.Y. Wang, X.Q. Wang, H.Z. Zhang, D.W. Song, L.Q. Zhang, and L.Y. Zhu, High-rate and long-life Ni-rich oxide cathode under high mass loading for sulfide-based all-solid-state lithium batteries, 138917, Copyright 2021, with permission from Elsevier.

structural deterioration occurs within the particles, thus resulting in the deactivation of the particles due to the loss of conductive contact and the accelerated decay of cycling performance [39–41]. Therefore, the electrochemical–mechanical effect of high-nickel layered cathode particles should not be ignored.

Liu *et al.* [32] compared the electrochemical performance of three different morphologies, namely, large polycrystalline (LP-NCM811), small-size polycrystalline (SP-NCM811), and single-crystalline (S-NCM811) NCM811 materials in sulfide SSE-based ASSLBs. As shown in Fig. 2(a), S-NCM811 provides a discharge capacity of $187 \text{ mAh}\cdot\text{g}^{-1}$ with coulombic efficiency (CE, η) of 74.0% at 0.1 C within 2.85–4.35 V; this value is higher than the $165 \text{ mAh}\cdot\text{g}^{-1}$ (CE = 67.9%) for SP-NCM811 or the $150 \text{ mAh}\cdot\text{g}^{-1}$ (CE = 67.6%) for LP-NCM811. Single-crystal NCM811 electrodes exhibit excellent cycling stability; compared with

SP-NCM811 and LP-NCM811, S-NCM811 has a superior rate performance and 54% capacity at 0.1 C despite discharging at a current density of 10 C. The researchers also used focused ion beam-scanning electron microscopy (FIB-SEM) to analyze the structural changes of the three NCM811 particles. The cross-sectional morphological changes of the single-crystal and polycrystalline NCM811 composite cathodes during the process and electrochemical cycling are shown schematically in Fig. 2(b), they found that the polycrystalline NCM811 ternary material showed significantly small cracks between the primary grains within the particles after being pressed into solid electrodes. The cracks between the primary grains within the particles increased and cracked after cycling, and the particles were broken into smaller polycrystalline materials. In contrast to polycrystalline NCM811, the single-crystal NCM811 ternary particles showed better structural integrity after being pressed into electrodes and

Table 1. Electrochemical properties of composite electrodes with high-nickel layered cathodes and SSEs

Composite cathode	SSE	Cell performance (discharge capacity)	Coulombic efficiency / %	Preparation methods	Ref.
NCM811/Li _{1.5} Al _{0.5} Ti _{1.5} (PO ₄) ₃ (LATP) = 70:30	LATP or β -Li ₃ PS ₄	145 mAh·g ⁻¹ (0.1 C), 2.65–4.35 V vs. Li ⁺ /Li (150°C)	80.5	Dry-mixing (mixed by hand and hot-press), 265 MPa	[30]
NCM622/Li ₆ PS ₅ Cl/super C65 = 69.1:29.6:1.3	Li ₆ PS ₅ Cl	155 mAh·g ⁻¹ (0.1 C), 2.50–4.25 V vs. Li ⁺ /Li (30°C)	81.5	Dry-mixing (mixed by hand), 370 MPa	[31]
NCM622/Li ₆ PS ₅ Cl/super C65/NBR binder = 68.1:29.2:1.3:1.4		133 mAh·g ⁻¹ (0.1 C), 2.50–4.25 V vs. Li ⁺ /Li (30°C)	73.8	Wet-slurry fabricated electrodes, 370 MPa	
NCM811(SC)/Li ₁₀ SnP ₂ S ₁₂ (LSPS)/acetylene black = 50:48:2	LSPS	187 mAh·g ⁻¹ (0.1 C), 2.85–4.35 V vs. Li ⁺ /Li (30°C); 120 mAh·g ⁻¹ (1 C)	88.8 (0.1 C)	Dry-mixing (mixed by mortar), 510 MPa	[32]
NCM90/Li _{9.54} Si _{1.74} P _{1.44} S _{11.7} Cl _{0.3} (LSPSC) = 73:27	LSPSC	156.1 mAh·g ⁻¹ (0.2 C), 2.7–4.28 V vs. Li ⁺ /Li (45°C); 110 mAh·g ⁻¹ (2 C)	77.9	Dry-mixing (mixed by hand), 245 MPa	[29]
NCM811/Li ₃ InCl ₆ (LIC) = 70:30	LIC	154 mAh·g ⁻¹ (0.1 C) 2.5–4.4 V vs. Li ⁺ /Li (25°C); 100 mAh·g ⁻¹ (2 C)	84.2	Dry-mixing (mixed by hand), 300 MPa	[23]
NCA80/Li ₆ PS ₅ Cl (LPSC)/super P = 70:40:3	LPSC	156 mAh·g ⁻¹ (0.1 C), 3.0–4.3 V vs. Li ⁺ /Li (30°C); 75 mAh·g ⁻¹ (2 C)	71.2	Dry-mixing (mixed by hand), 370 MPa	[33]
FCG75/LPSC/super P = 70:30:3		196 mAh·g ⁻¹ (0.1 C), 3.0–4.3 V vs. Li ⁺ /Li (30°C); 145 mAh·g ⁻¹ (2 C)	84.9		
NCM85/Li ₆ PS ₅ Cl (LPSC)/C = 85:13:2 (0–1wt% PTFE)	LPSC	203 mAh·g ⁻¹ (0.05 C), 2.53–4.23 V vs. Li ⁺ /Li (30°C)	89	Dry-film process (PTFE binder), 300 MPa	[34]
NCA88/Li ₃ YCl ₆ (LYC)/super P = 60:40:3	LYC	199 mAh·g ⁻¹ (0.1 C); 130 mAh·g ⁻¹ (4 C), 3.0–4.3 V vs. Li ⁺ /Li (30°C)	89.6 (0.1 C)	Dry-mixing (mixed by hand), 370 MPa	[35]
NCA88/LYC/super P = 70:30:3		201 mAh·g ⁻¹ (0.1 C); 32 mAh·g ⁻¹ (4 C), 3.0–4.3 V vs. Li ⁺ /Li (30°C)	87.7 (0.1 C)		
NCA80/LSPC/acetylene black = 39.2:57.2:3.6	Li ₆ PS ₅ Cl	140 mAh·g ⁻¹ (370 MPa, 0.1 C), 3.0–4.3 V vs. Li ⁺ /Li (30°C)	67	Dry-mixing (mixed by hand), 5–370 MPa	[36]
		128 mAh·g ⁻¹ (25 MPa, 0.1 C), 3.0–4.3 V vs. Li ⁺ /Li (30°C)	65		
NCM622/Li ₂ S–P ₂ S ₅ /super C65/NBR binder = 70:27.5:1.0:1.5	Li ₂ S–P ₂ S ₅	153 mAh·g ⁻¹ (0.05 C), 2.9–4.3 V vs. Li ⁺ /Li (30°C); 90 mAh·g ⁻¹ (1 C)	84	Wet chemical process, sheet-type composite electrodes, 370 MPa	[37]

Note: NCM—LiNi_xMn_yCo_{1-x-y}O₂; NBR—Nitrile rubber; PTFE—Polytetrafluoroethylene.

more uniform volume change during the charge and discharge cycle. The particles are structurally intact and could maintain good solid–solid contact with the solid electrolyte and conductive agent. Han *et al.* [35] also performed a comparative analysis between single-crystal and polycrystalline LiNi_{0.88}Co_{0.11}Al_{0.01}O₂ (NCA88) in Li₃YCl₆ halide SSEs and Li₆PS₅Cl_{0.5}Br_{0.5} SSEs and concluded that the single-crystal high-nickel layered cathode without cracks and particle fragmentation had better first pair performance in both electrolytes.

Improving the particle structure stability of polycrystalline materials will enhance their electrochemical performance in SSEs. Jung *et al.* [33] chose Li[Ni_{0.75}Co_{0.10}Mn_{0.15}]O₂ (FCG75), which consists of radially oriented rod-shaped particles at full concentration gradient, and conventional Li[Ni_{0.80}Co_{0.16}Al_{0.04}]O₂ (NCA80), which has randomly ori-

ented grains, and compared FCG75/Li₆PS₅Cl and NCA80/Li₆PS₅Cl materials under sulfide ASSLBs. The FCG75 with radially oriented rod-shaped particles showed superior electrochemical performance at different degrees in terms of reversible capacity (196 vs. 156 mAh·g⁻¹), initial CE (84.9% vs. 71.2%), and capacity retention (79.1% vs. 46.9% after 200 cycles) at 30°C [33]. Polycrystalline FCG75 is a secondary particle agglomerate with special morphology consisting of primary lamellar particles, which have a high percentage of exposed (100) or (010) planes along the [003] direction and are radially aligned closely to the center point of the sphere. Owing to its unique internal particle structure design, this material can provide the excellent electrochemical properties of polycrystalline high-nickel layered cathodes in solid-state batteries. The particles maintain mechanical integrity during charge and discharge cycles [42]. Other ways to im-

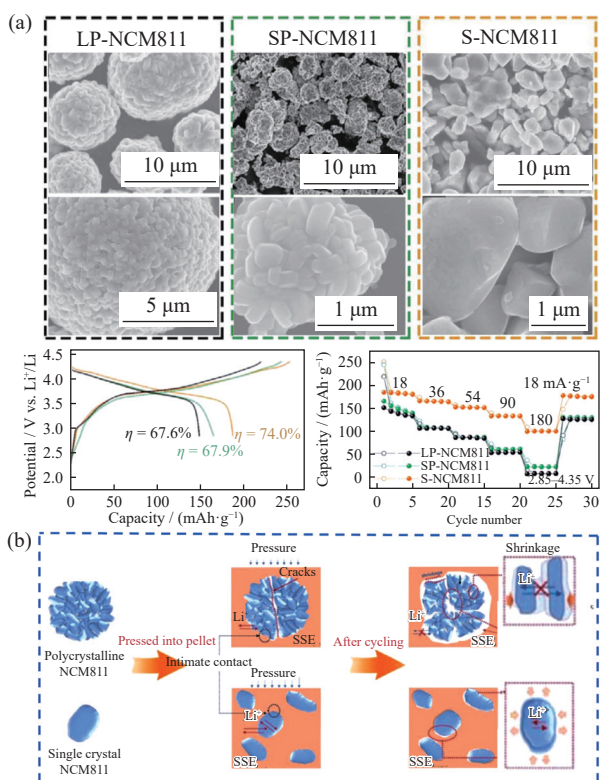


Fig. 2. (a) Scanning electron microscopy (SEM) images of high-nickel layered cathode structures with LP-NCM811, SP-NCM811, and S-NCM811 microstructures and their first charge/discharge curves and rate performance. (b) Schematic of the morphological changes in the cross section of single-crystal and polycrystalline NCM811 composite cathodes during the pressure of electrodes and charge/discharge cycling. X.S. Liu, B.Z. Zheng, J. Zhao, W.M. Zhao, Z.T. Liang, Y. Su, C.P. Xie, K. Zhou, Y.X. Xiang, J.P. Zhu, H.C. Wang, G.M. Zhong, Z.L. Gong, J.Y. Huang, and Y. Yang, *Adv. Energy Mater.*, vol. 11, 2003583 (2021) [32]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

prove the particle mechanics of high-nickel layered cathodes include cladding and doping. In summary, the internal structural integrity of high-nickel layered cathode particles is one of the influencing factors for ASSLBs [43–44].

2.2. Electrochemical properties under different preparation parameters

The original goal in the preparation of high-nickel layer cathode and SSEs is to ensure the good ion contact and ion conductivity of SSEs. High-nickel layered cathodes with sulfide or halide SSEs are usually prepared using “dry-mixing” and “wet-mixing” methods. “Dry-mixing” is a common experimental preparation method of solid-state batteries in which the active substance, SSE, and conductive agent are dried in a predetermined proportion and mixed in agate mortar without polymer binder (Fig. 3(a)) [31]. Researchers have added a binder to the traditional “dry-mixing” method, blended all the materials well, and then prepared the poles under a certain pressure to assemble solid-state soft pack batteries (Fig. 3(b)) [34]. “Wet-mixing” requires simultaneous experimentation or research to detect anhydrous solvents (weakly

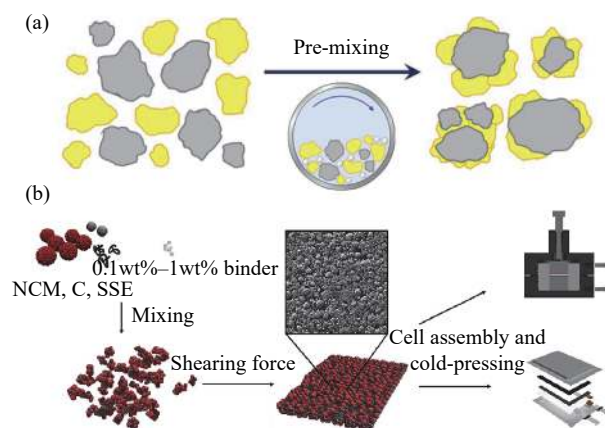


Fig. 3. (a) Schematic of composite electrode prepared through the mechanical grinding of NCM622 and SSE powder. (b) Schematic of dry electrode prepared on NCM, C, SSE, and PTFE binder. (a) Reprinted from *J. Power Sources*, 375, Y.J. Nam, D.Y. Oh, S.H. Jung, and Y.S. Jung, Toward practical all-solid-state lithium-ion batteries with high energy density and safety: Comparative study for electrodes fabricated by dry- and slurry-mixing processes, 93–101, Copyright 2018, with permission from Elsevier. (b) Reprinted from *Energy Storage Mater.*, 21, F. Hippauf, B. Schumm, S. Doerfler, H. Althues, S. Fujiki, T. Shiratsuchi, T. Tsujimura, Y. Aihara, and S. Kaskel, Overcoming binder limitations of sheet-type solid-state cathodes using a solvent-free dry-film approach, 390–398, Copyright 2019, with permission from Elsevier.

polar xylenes and alkanes) that create minor damage to the active material and SSE. A slurry consisting of the active material, SSE, conductive agent, and binder is wet-mixed in the anhydrous solvent [37,45]. The prepared slurry is then coated on the aluminum or nickel foil collector and dried under a vacuum at a suitable temperature. The obtained sheet electrodes show good adhesion on the collector [37]. Oxide SSEs are prepared differently from sulfide and halide SSEs and usually require methods such as retreating to create close contact between the active material and SSE; spraying and vapor deposition are also methods for preparing composite anodes [46–48]. In conclusion, good contact between the active material and SSE is crucial in the preparation of composite electrodes with high-nickel layered cathodes and SSEs; irreversible damage during preparation must be prevented to ensure the ionic conductivity of the SSE [49–50].

In the composite electrodes of high-nickel ASSLBs, the spatially uniform contact between the high-nickel layered cathode and SSE, the effect of pressure, and the conductive agent binder affect the electrochemical properties of the SSEs. The solid–solid contact between the cathode and the SSE poses more difficulties in preparing composite electrodes than that in liquid batteries, which require spatially uniform distribution between the active material and SSE to achieve the excellent electrochemical performance of the material [51–53]. Spatially uniform distribution involves many aspects, such as the type, size, and morphology of the active material and SSE material, the ratio of the active material to the SSE, and the preparation method of the electrode. Fig. 4(a) shows the difference in the electrochemical perform-

ance of single-crystal NCA matched with Li_7YCl_6 halide SSEs at different ratios [35]. The overabundance of SSE (40.7wt%) led to significant improvement in cycling and multiplicative performance. When the content of LYC in the composite electrode is 29.1wt%, contact loss between NCA particles and LYC has likely occurred during charging and discharging. Meanwhile, for the LYC ratio of 40.7wt%, the

surface coverage of LYC on individual NCA is relatively uniform, the contact between NCA and LYC is relatively close during cycling, and the cracking of NCA particles is relatively minor, all of which led to an excellent electrochemical performance [36]. Unique dry impact mixing has also been used for the preparation process and can provide uniform contact between the SSE and cathode particles.

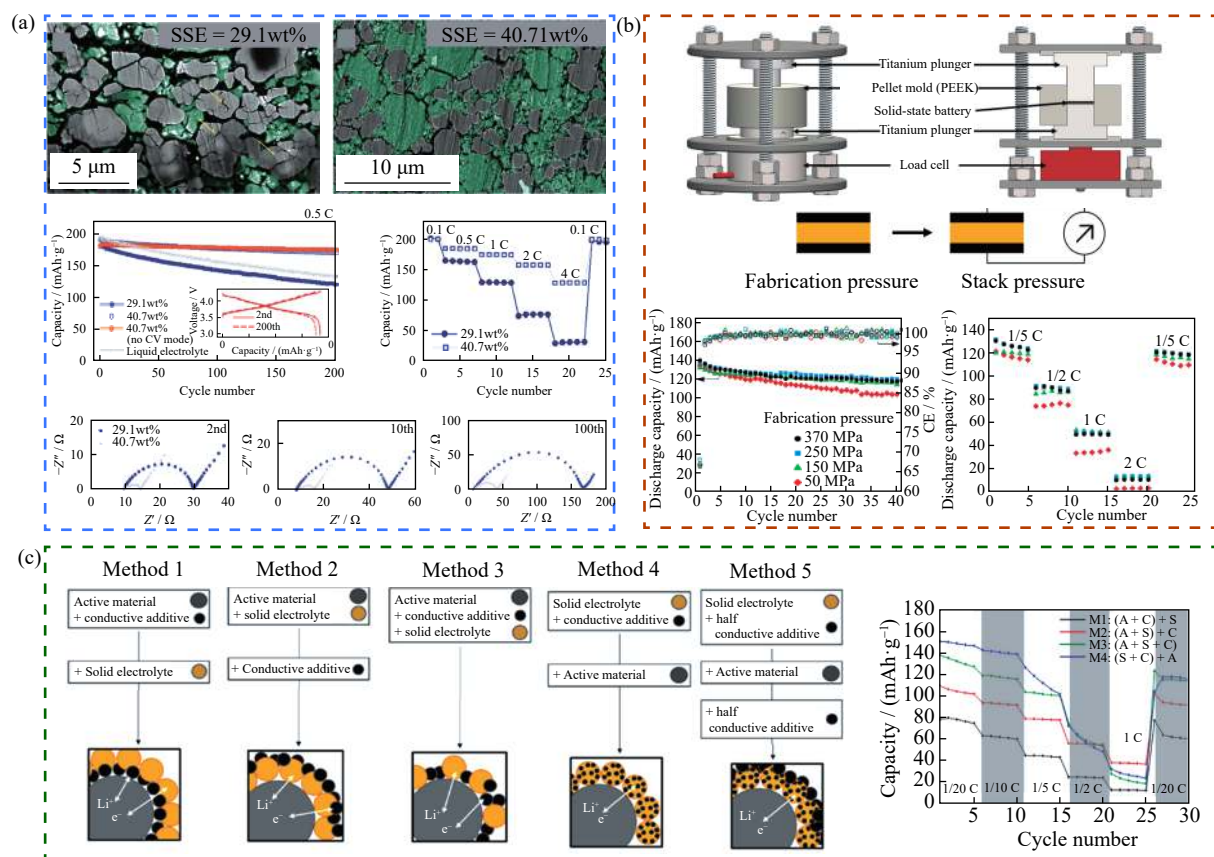


Fig. 4. (a) Cross-sectional SEM-(backscattered electron) BSE images of S/LYC electrodes with LYC contents of 29.1wt% and 40.7wt% after the first discharge to 3.0 V (compared with Li/Li⁺) and comparison of 200-cycle performance, rate performance, and impedance change during cycling. CV represents constant voltage. (b) Comparison of cycling performance and rate performance of LiIn | LPSC | NCA cells prepared under different preparation pressures. (c) Protocols for five different hybrid methods, expected microstructure of the resulting composite cathodes, and rate capability of all-solid-state cells prepared by hybrid methods M1–M4. (a) Y. Han, S.H. Jung, H. Kwak, S. Jun, H.H. Kwak, J.H. Lee, S.T. Hong, and Y.S. Jung, *Adv. Energy Mater.*, vol. 11, 2100126 (2021) [35]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission. (b) Reproduced from Ref. [36] with permission from the Royal Society of Chemistry. (c) Reprinted by permission from Springer Nature: *J. Electroceram.*, Importance of mixing protocol for enhanced performance of composite cathodes in all-solid-state batteries using sulfide solid electrolyte, S. Noh, W.T. Nichols, M. Cho, and D. Shin, Copyright 2018.

Pressure is a vital parameter in ASSLBs. For composite electrodes, pressure affects the state of particles such as active materials and SSEs, the contact between the active material and SSE, the apparent ionic conductivity of SSEs and cell impedance, and many other aspects [54–56]. Fig. 4(b) shows the electrochemical performance of LiIn | $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSC) | NCA ASSLBs prepared at different pressures in the composite electrode at 25 MPa [36]. At a low fabrication pressure (50 MPa), the composite electrode cathode has many voids in contact with the electrolyte, which are detrimental to the cell performance. ASSLBs prepared at relatively high preparation pressure (370 MPa) exhibit better performance and significantly higher capacity retention and rate capability than

the other prepared batteries. The cathode material and SSE are prepared with a certain critical pressure. The use of excessive pressure will lead to the fragmentation of the particles, thus affecting the performance.

Appropriate additives are required to achieve the good performance of SSE composite electrodes. The addition of conductive agents can enhance the effective charge transfer in the interstitial region of the composite electrode [57–59]. In general, the number of additives must be limited to a certain point to achieve high energy density; however, the design of composite cathode becomes highly complicated [60]. Noh *et al.* [51] tested a mixing scheme of five conductive additives and found that the initial discharge capacity and

rate capability varied significantly with the order of mixing in Fig. 4(c). The mixing scheme of mixing conductive additives at the active particle interface reduced the ability to increase electron conductivity, leading to a decrease in interfacial resistance.

3. High-nickel layered cathode and SSE interface

For composite electrodes with high-nickel layered cathodes and SSEs, the interface between the high-nickel layered cathode and SSE is the channel for ions and electrons to enter the active material and affects the electrochemical performance of ASSLBs [61]. In the following section, the interfacial reaction and contact loss between the high-nickel layered cathode and SSE are reviewed, and practical solutions for the interfacial problem are presented in Section 3.3.

3.1. Space-charge layers (SCLs)

The presence of SCLs in all-solid-state cells is one of the reasons for the slow transport in the solid electrode/electrolyte interface; however, the current understanding of the SCL is limited. At the cathode/SSE interface, the charged material (i.e., atoms or electrons) is driven toward the material with the lowest chemical potential (highest voltage) due to the difference in potential between the two sides of the interface. As a result, a charge accumulation zone is formed at the interface, a phenomenon known as the SCL effect. The cathode exhibits an insulating state with high lithium content in the material at the early stage of charging, and the formation of the SCL at the cathode/electrolyte interface is one of the main reasons for the high interfacial impedance of ASSLBs. The existence of the SCL was also confirmed by experimentally measuring the charge aggregation phenomenon at the interface [62]. This SCL effect is also present in solid-state cells

matched with high-nickel layered cathodes and inorganic SSEs and is represented as an unusual slope at the beginning of the charge curve or an indirect increase in interfacial impedance [63]. Zhang *et al.* [64] analyzed the SCL effect in NCM811/Li₆PS₅Cl/Li ASSLBs by *in-situ* electrochemical impedance spectroscopy (EIS) and *in-situ* Raman spectroscopy measurements. Fig. 5(a) shows the *in-situ* EIS profile during the first week of charging and the equivalent circuit fit of the EIS profile during two weeks of charging and discharging the NCM811/LPSC solid-state battery measured at 0.2 C current density and 2 mAh·g⁻¹ equivalent capacity. After the equivalent circuit was fitted, R_{ct2} , which represents the interfacial impedance of NCM811 and LPSC, exhibited a high interfacial impedance at the beginning of the initial charge and the end of charge; this finding is consistent with the impedance change pattern of solid-state batteries caused by SCLs [64]. Fig. 5(b) depicts the migration and concentration distribution of Li⁺ at the interface before/after the charge and during the charge–discharge process. In the initial stage of charging, the migration of Li⁺ from the Li₆PS₅Cl side is more limited than that from the NCM due to the diffusion barrier of the SCL. This phenomenon causes a large amount of Li ions to accumulate on the NCM side, thereby leading to a high interfacial impedance at the initial stage of charging. As the charging proceeds, the concentrations on both sides become stable, and the migration of Li⁺ reaches dynamic equilibrium, indicating SCL stability. In the discharge process, the concentration distribution of Li⁺ shows the opposite trend to the above impedance change due to the migration of Li⁺ in the opposite direction. During charging and discharging, the concentration distribution and SCL change periodically. Given that the SCL is redistributed after the first week of charging, the effect caused by the SCL effect is reduced in the second week. The SCL effect is one of the main reasons for the change in the interfacial impedance of solid-state cells at the

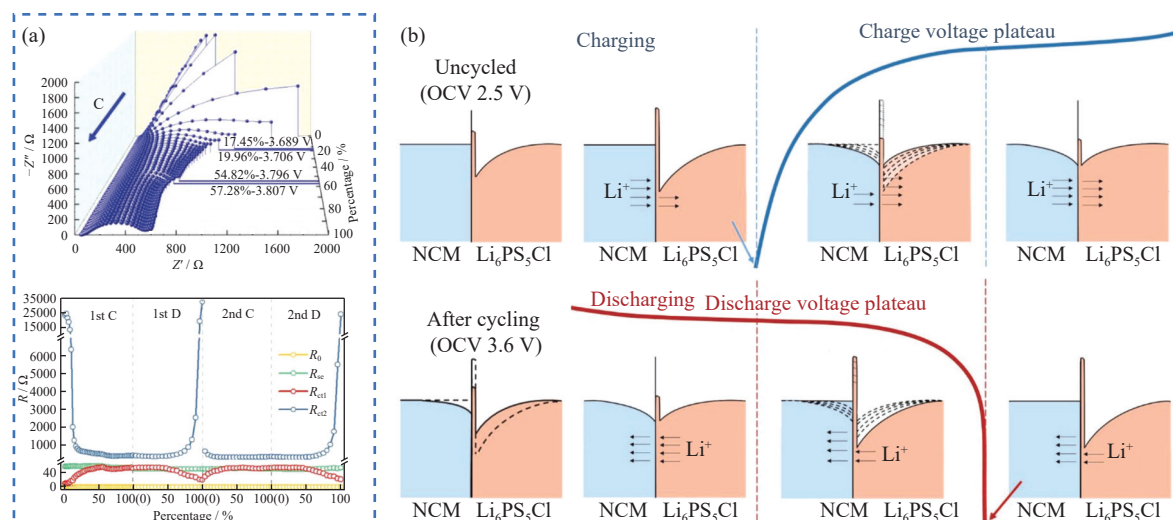


Fig. 5. (a) Variation of *in-situ* impedance spectra and fitted resistance values of NCM/Li₆PS₅Cl/Li cells at 0.2 C and 2 mAh·g⁻¹ for the initial charge. R_0 , R_{se} , and R_{ct1} and R_{ct2} represent the current collector resistance, the bulk resistance, and the two interfacial resistances. (b) Schematic of the migration of Li⁺ concentration in the SCL at the NCM/Li₆PS₅Cl interface. OCV represents open circuit voltage. J. Zhang, C. Zheng, L.J. Li, Y. Xia, H. Huang, Y.P. Gan, C. Liang, X.P. He, X.Y. Tao, and W.K. Zhang, *Adv. Energy Mater.*, vol. 10, 1903311 (2020) [64]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

beginning of the cycle.

3.2. Interfacial reactions

High-nickel layered cathodes typically operate in 2.5–4.3 V (Li^+/Li) or even higher voltage range. Most sulfide SSEs and oxide SSEs are not stable at high voltages and could oxidize to other compounds with low lithium-ion conductivity, thereby increasing interfacial impedance [65–67]. Zhu *et al.* [68] reported that some sulfide SSEs also have low thermodynamic oxidation potentials, such as $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) at 2.14 V, Li_3PS_4 at 2.31 V, $\text{Li}_6\text{PS}_5\text{Cl}$ at 2.01 V, and $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$ at 3.1 V. By contrast, sulfides are thermodynamically unstable at high voltages and are highly susceptible to oxidation reactions. At high voltages, $\text{Li}_6\text{PS}_5\text{Cl}$ oxidizes to monosulfide, lithium polysulfide, P_2S_x ($x < 5$), phosphate, and LiCl ; meanwhile, the oxidation products of LGPS are Li_3PS_4 , S, and GeS_2 [69]. These oxidation products at high voltages tend to accumulate at the interface between the high-nickel layered cathode and SSE, resulting in a decrease in capacity and an increase in impedance during ASSLB cycling. In addition, oxide SSEs have thermodynamically stable oxidation potentials primarily below 4.3 V. Among these, the garnet-type LLZO SSE has a thermodynamic oxidation potential of 2.9 V, and its oxidation products are Li_2O_2 , La_2O_3 , La_2ZrO_7 , La_6ZrO_7 , and O_2 [48].

Interfacial reactions also occur in the interface between the high-nickel layered cathode and SSE, resulting in material exchange. Banerjee *et al.* [70] used NCA charged to 4.3 V in a liquid cell and mechanically mixed it with an LPSC SSE. Experiments and calculations revealed the spontaneous reaction of LPSC in the NCA interface, as shown in Fig. 6(a). The X-ray powder diffraction (XRD) pattern shows the formation of LiCl , Ni_3S_4 , Li_3PO_4 , and other unknown phases in the reaction between the active material and electrolyte. In addition, small amounts of Ni_3S_4 or NiS_2 and the partial oxidation of S and P elements were observed. The researchers tested the mixture of uncharged NCA and LPSC but did not obtain similar results, thus further proving that the charged state of NCA has a higher oxidation state and is more active than the original NCA. This study also used ab initial molecular dynamics to simulate the interfacial dynamics between NCA and LPSC in the 50% state of charge at 300 K. The calculation results for the formation of P–O, M–S ($\text{M} = \text{Co}, \text{Ni}$), S–S, and LiCl bonds at the interface were consistent with the experimental results. Oxide SSEs usually require a high-temperature treatment to enhance the solid–solid contact between composite electrodes due to their mechanical stiffness and high crystal boundary resistance; however, interfacial reactions may occur between the high-nickel layered cathode and oxide SSE during this process [71]. As shown in

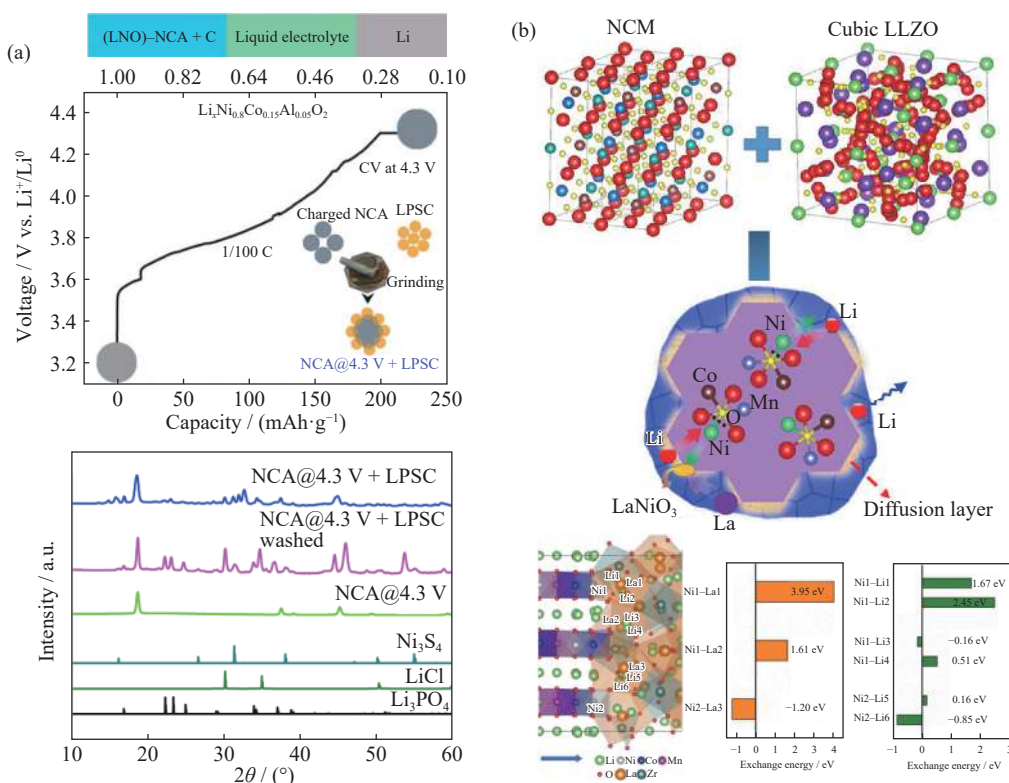


Fig. 6. (a) Potential profiles NCA charged in a liquid cell and XRD patterns of NCA and LPSC after grinding in the fully charged state compared with reference compounds. (b) Schematic of the reaction between NCM and LLZO surface layers during ball milling and cofiring. (a) Reprinted with permission from A. Banerjee, H.M. Tang, X.F. Wang, J.H. Cheng, H. Nguyen, M.H. Zhang, D.H.S. Tan, T.A. Wynn, E.A. Wu, J.M. Doux, T.P. Wu, L. Ma, G.E. Sterbinsky, M.S. D'Souza, S.P. Ong, and Y.S. Meng, *ACS Appl. Mater. Interfaces*, vol. 11, 43138–43145 (2019) [70]. Copyright 2019 American Chemical Society. (b) Reprinted with permission from N. Zhang, X.H. Long, Z. Wang, P.F. Yu, F.D. Han, J.M. Fu, G.X. Ren, Y.R. Wu, S. Zheng, W.C. Huang, C.S. Wang, H. Li, and X.S. Liu, *ACS Appl. Energy Mater.*, vol. 1, 5968–5976 (2018) [72]. Copyright 2018 American Chemical Society.

Fig. 6(b), Zhang *et al.* [72] used the NCM/LLZO interface model to calculate the reactions between Ni–La and Ni–Li at the interface. Energies of -1.20 and -0.85 eV were obtained for Ni–La and Ni–Li, respectively, implying the feasibility of some degree of atomic exchange at the NCM/LLZO interface. The atomic exchange at the interface can induce the decomposition of LLZO to form $\text{La}_2\text{Zr}_2\text{O}_7$ and LaNiO_3 , and this phenomenon intensifies with the increasing temperature. The formation of LaNiO_3 at the interface is one of the reasons for the poor capacity of NCM in LLZO SSEs.

Halide SSEs with high ionic conductivity at room temperature ($10^{-3} \text{ S}\cdot\text{cm}^{-1}$), wide electrochemical window and high oxidation potential ($>4 \text{ V}$), and good compatibility with cathode materials have been initially matched with high-nickel layered cathodes; their good performance has attracted great interest for their application in ASSLBs [73].

Most stable Li_3MCl_6 SSEs exhibit oxidation potentials above 4.2 V , and typical high-nickel layered cathodes operate at potentials between 2.8 and 4.3 V . Li_3MCl_6 can also be

applied to high-nickel layered cathodes [74]. As shown in Fig. 7, Park *et al.* [75] calculated the reaction energy of Li_3MCl_6 with LiCoO_2 (LCO), LiMn_2O_4 (LMO), LiFePO_4 (LFP), and NMC. Compared with sulfide solid electrolytes, the chemical reaction energy between Li_3MCl_6 and oxides is low. In particular, Li_3MCl_6 has less than $100 \text{ meV}\cdot\text{atom}^{-1}$ chemistry energy with NMC and even low reactivity with LMO ($\sim 30 \text{ meV}\cdot\text{atom}^{-1}$), LFP ($\sim 40 \text{ meV}\cdot\text{atom}^{-1}$), and LCO ($\sim 50 \text{ meV}\cdot\text{atom}^{-1}$). However, Li_3MCl_6 is still reactive with NMC and is unstable at high potentials ($>4.5 \text{ V}$), thus leading to chemical decomposition at the interface [66]. This calculation predicts the oxidation products between NMC and Li_3MCl_6 , the possible interfacial reaction products between NMC and LYC, such as YClO , NiCl_2 , Co_3O_4 , and LiCl , and the possible interfacial reaction products between NMC and LIC, such as $\text{Li}_2\text{Mn}_3\text{NiO}_8$, NiO , Co_3O_4 , In_2O_3 , and LiCl . To date, the interfacial behavior between Li_3MCl_6 SSEs and high-nickel layered cathodes has not been experimentally verified and thus requires relevant experiments and calculations.

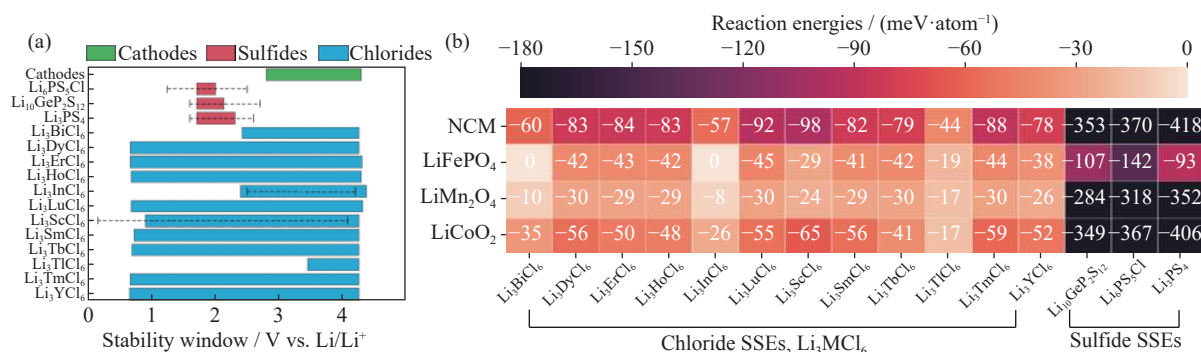


Fig. 7. (a) Calculations of thermodynamic electrochemical stability windows under Li_3MCl_6 SSEs and sulfide SSEs. (b) Thermal plots of the maximum reaction energies for twelve Li_3MCl_6 SSEs, three lithium sulfide SSEs, and four cathode materials (LCO, LMO, LFP, and NMC). Reprinted with permission from D. Park, H. Park, Y. Lee, S.O. Kim, H.G. Jung, K.Y. Chung, J.H. Shim, and S. Yu, *ACS Appl. Mater. Interfaces*, vol. 12, 34806–34814 (2020) [75]. Copyright 2020 American Chemical Society.

3.3. Contact loss of the interface between the SSE and high-nickel layered cathode

Mechanical problems (contact loss and fracture) arising in composite electrodes can affect the cell microstructure, which in turn influences the performance of ASSLBs [76–77]. The deformation of the high-nickel layered cathode during Li^+ de-embedding affects the electrochemical strain of the composite electrode. During the charging of the high-nickel layered cathode, the size of the Ni ions decreases from Ni^{2+} to Ni^{4+} ; this effect is overcompensated by the Coulomb repulsion on the anisotropy, leading to the simultaneous contraction of the a - and c -axes [78]. X-ray diffraction combined with refinement analysis revealed that the volume of the NCM851005 (85% nickel) material decreases by approximately 6.0% after charging to 4.3 V and by approximately 8.0% after charging to 4.6 V [79]. Fig. 8(a) shows the change in cell volume and molar volume versus lithium content for several typical materials [80]. The graph clearly shows that the volume of the high-nickel layered cathode decreases significantly during the de-lithium process. Owing to the force

deformation of the electrolyte material, the stress caused by volume changes in high-nickel layered cathodes can cause local stresses, accompanied by harmful consequences such as crack formation and extension, interface delamination, and/or loss of contact between particles. High-nickel layered cathodes suffer from a degree of mechanical contact loss whether matched to oxide SSEs with high Young's modulus or to sulfide and halide SSEs with low Young's modulus.

Koerver *et al.* [80] chose NCM811 materials and $\beta\text{-Li}_3\text{PS}_4$ SSEs with $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_7\text{Ti}_5\text{O}_{12}$ (LTO) as the negative electrode. The anode with zero-strain LTO was used to ignore the effect of the anode on cell pressure. The pressure of the assembled LTO/SSE | SSE | NCM811/SSE can indicate the influence of the composite positive electrode. After NCM811 reached the charged state, it experienced a 6% contraction of cell volume, which in turn produced a tensile pressure of $p(\text{NCM/LTO}) = -42.7 \text{ MPa}$. This experiment shows that the ASSLB pressure decreases due to the volume contraction of the high-nickel layered cathode during charging. As shown in Fig. 8(c), Koerver *et al.* [81] used SEM to study NCM811 matched with $\beta\text{-Li}_3\text{PS}_4$ in ASSLB and found that the active

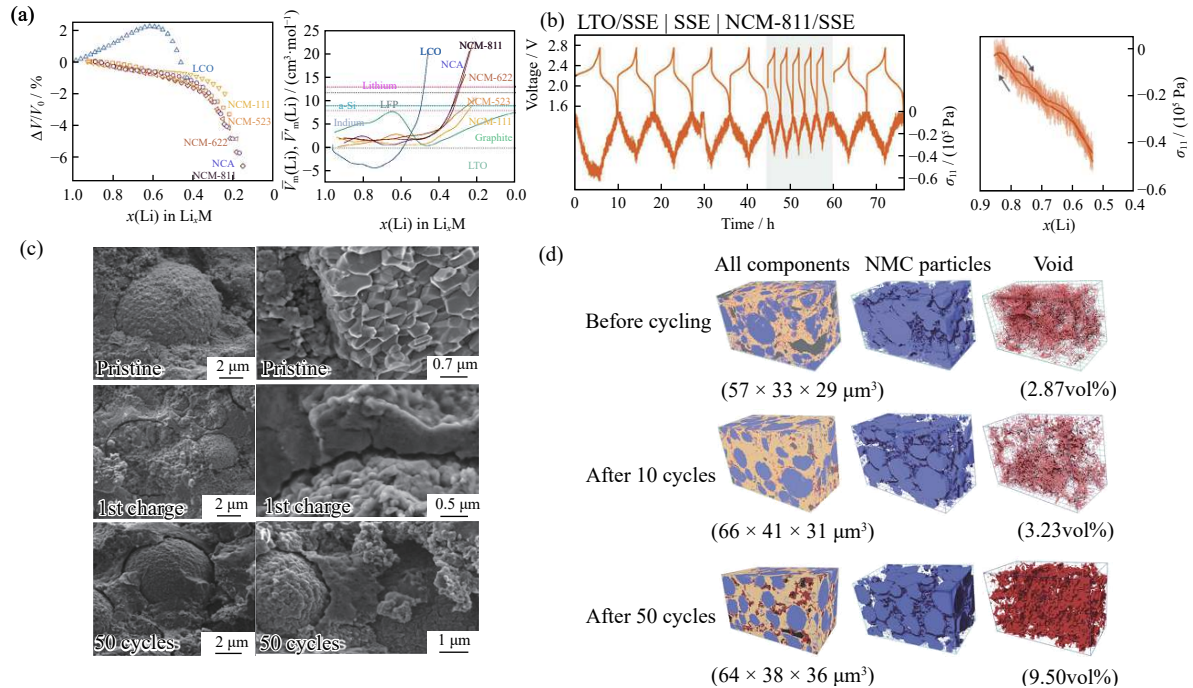


Fig. 8. (a) Volume change data of several common cathode materials (LCO, NCM, and NCA) during lithium-ion de-embedding. $\Delta V/V_0$, $\bar{V}_m(\text{Li})$, and $\bar{V}'_m(\text{Li})$ represent the volumetric strain, the partial molar volume of Li in homogeneous storage phases, and the apparent partial molar volume in two-phase electrode materials, respectively. (b) LTO/SSE | SSE | NCM811/SSE battery pressure change during charging and discharging. σ_{11} represents the net stress of NCM811/LTO. (c) SEM of composite electrode cross section of Li-In | $\beta\text{-Li}_3\text{PS}_4$ | NCM811/ $\beta\text{-Li}_3\text{PS}_4$ cell before cycling, after the first cycle, and after 50 cycles. (d) Reconstructed 3D structures of $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2/75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$ cathode composites before cycling, after 10 cycles, and after 50 cycles [82]. (a, b) Reproduced from Ref. [80] with permission from the Royal Society of Chemistry. (c) Reprinted with permission from R. Koerver, I. Aygün, T. Leichtweiß, C. Dietrich, W.B. Zhang, J.O. Binder, P. Hartmann, W.G. Zeier, and J. Janek, *Chem. Mater.*, vol. 29, 5574-5582 (2017) [81]. Copyright 2017 American Chemical Society.

material exhibited chemical-mechanical contraction during charge and discharge; this phenomenon resulted in the loss of contact between the SSE and NCM811. Shi *et al.* [82] used FIB-SEM for the 3D characterization of the composite electrode morphology of the NMC cathode ($\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$) before and after cycling with an amorphous $75\text{Li}_2\text{S}-25\text{P}_2\text{S}_5$ (LPS) SSE as shown in Fig. 8(d). The imaging data showed that the contact loss between the cathode material and SSE increased with the number of cycles. The volume occupancy of the blank area within the electrode was 2.87% before the cycle and then increased to 9.50% after 50 cycles. The empty area was mostly distributed on the surface of the cathode material particles, and a contact area loss of more than 10% was observed. The equivalent circuit fitting of the EIS measurements after the first cycle, 10 cycles, and 50 cycles revealed that the resistance corresponding to the medium frequency region at the solid-solid interface of the cathode and electrolyte increased from 954 Ω in the first cycle to 1241 Ω after 10 cycles (30% increase) and further increased to 3283 Ω after the 50 cycles (244% increase). This result indicates that the contact loss at the solid-solid interface also increases the interfacial impedance.

3.4. Optimization method for the interface between the SSE and high-nickel layered cathode

Interfacial degradation in the composite electrodes of sol-

id-state batteries is mainly caused by interfacial reactions and contact problems. Surface-coated high-nickel layered cathodes have received wide attention due to their ability to improve the solid-solid interface properties in inorganic SSEs [83–84]. The preferred option is to construct a buffer layer on the surface of the active material because cladding the electrolyte usually increases the interfacial impedance. Surface clad materials must exhibit the following: (1) a wide electrochemical window, with electrochemical stability within the stable potential window of high-nickel layered cathodes and inorganic SSEs; (2) a high chemical stability; (3) a certain lithium-ion transport capability to form a good lithium-ion transport channel between high-nickel layered cathodes/inorganic SSEs; (4) a low electronic conductivity, which can prevent the electrochemical decomposition of inorganic electrolytes on the surface of high-nickel layered cathodes; (5) uniform cladding [83]. Materials such as LiNbO_3 [85–86], LiTaO_3 [87], Li_2ZrO_3 [88], and Li_3PO_4 [24] have been applied as cladding materials for active materials due to their chemical stability in a wide potential range (2–4 V). In addition to oxides, polyatomic compounds such as LiH_2PO_4 , $\text{LiH}_2\text{PO}_4(\text{PO}_4)_3$, and LiPO_3 have been proven to be excellent coating layer materials through calculations and experiments. Lithium borate and halides also exhibit excellent (electro)chemical stability at the interface [83]. Table 2 lists the optimized high-nickel layered cathodes and their electro-

Table 2. Modified high-nickel layered cathodes and electrochemical properties in ASSLBs

Cathode	SSE	Discharge capacity	Cycle performance	Methods	Ref.
Diamond-like carbon (DLC) coating–LiNi _{0.8} Co _{0.15} Al _{0.05} O ₂	Li ₂ S–P ₂ S ₅	120.7 mAh·g ⁻¹ (0.1 C), 2.5–4.0 V vs. Li ⁺ /Li (25°C)	(0.1 C charge/0.5 C discharge) 100th/93%	Chemical vapor deposition (CVD)	[89]
Ti-containing surface layer–LiNi _{0.8} Co _{0.15} Al _{0.05} O ₂	Li ₁₀ GeP ₂ S ₁₂	122 mAh·g ⁻¹ (0.1 C), 2.5–4.4 V vs. Li ⁺ /Li (25°C)	(0.1 C) 100th/94%	Sol–gel method	[90]
Li ₂ CO ₃ /LiNbO ₃ -coated NCM622	β-Li ₃ PS ₄	148 mAh·g ⁻¹ (0.1 C), 3.0–4.3 V vs. Li ⁺ /Li (25°C)	(0.1 C) 100th/91%	Liquid phase coating	[91]
Li ₃ PO ₄ (LPO)-coated NMC811	Li ₁₀ GeP ₂ S ₁₂	163.2 mAh·g ⁻¹ (0.2 C), 2.5–4.5 V vs. Li ⁺ /Li (25°C)	(0.2 C) 300th/60%	Atomic layer deposition (ALD)	[24]
Li ₂ ZrO ₃ -coated NCM622	Li ₇ P ₂ S ₈ I	143.7 mAh·g ⁻¹ (0.05 C), 3.0–4.3 V vs. Li ⁺ /Li (25°C)	(0.05 C) 20th/95%	Resonant acoustic mixer	[92]
LiNbO ₃ -coated NCM622		146.7 mAh·g ⁻¹ (0.05 C), 3.0–4.3 V vs. Li ⁺ /Li (25°C)	(0.05 C) 20th/90%		
(Li ₂ O–ZrO ₂)-coated NCM811	Li ₆ PS ₅ Cl	210 mAh·g ⁻¹ (0.2 C), 146 mAh·g ⁻¹ (0.5 C), 2.5–4.25 V vs. Li ⁺ /Li (60°C)	(0.5 C) 1000th/89%	Dry film process and Ag–C nanocomposite anode	[93]
LiNbO ₃ -coated NCM811	Li ₁₀ GeP ₂ S ₁₂	162 mAh·g ⁻¹ (0.1 C), 136.8 mAh·g ⁻¹ (0.5 C), 2.7–4.38 V vs. Li ⁺ /Li (25°C)	(0.5 C) 50th/77.9%	Liquid phase coating	[94]
Li ₂ CO ₃ /LiNbO ₃ -coated NCM811	Li ₁₀ GeP ₂ S ₁₂	182.5 mAh·g ⁻¹ (0.1 C), 103.6 mAh·g ⁻¹ (3 C), 2.7–4.38 V vs. Li ⁺ /Li (35°C)	(0.3 C) 585th/80%	Liquid phase coating	[86]
Li ₂ ZrO ₃ -coated NCM622	Li ₆ PS ₅ Cl	170 mAh·g ⁻¹ (0.2 C), 110 mAh·g ⁻¹ (1 C), 2.5–4.38 V vs. Li ⁺ /Li (45°C)	(0.2 C) 60th/69%	Liquid phase coating	[88]
LiTaO ₃ -coated NCM811	Li ₆ PS ₅ Cl	199.8 mAh·g ⁻¹ (8.5 mA·g ⁻¹), 122.5 mAh·g ⁻¹ (51 mA·g ⁻¹), 2.5–4.4 V vs. Li ⁺ /Li (30°C)	(34 mA·g ⁻¹) 30th/83%	Precursor-based liquid phase coating	[87]
LiNbO ₃ -coated NCM811		195.7 mAh·g ⁻¹ (8.5 mA·g ⁻¹), 127.3 mAh·g ⁻¹ (51 mA·g ⁻¹)	(34 mA·g ⁻¹) 30th/82%	Post liquid phase coating	
Al-modifying layer-NCM90	Li _{0.54} Si _{1.74} P _{1.44} S _{11.7} Cl _{0.3} (LSPSC)	158.6 mAh·g ⁻¹ (0.2 C), 124.7 mAh·g ⁻¹ (1 C), 2.7–4.3 V vs. Li ⁺ /Li (45°C)	(1 C) 500th/96.3%	Core–shelled NCM90, liquid phase coating	[29]
Li ₂ CO ₃ /LiNbO ₃ -coated NCM622	Li ₆ PS ₅ Cl	180 mAh·g ⁻¹ (0.2 C), 2.7–4.45 V vs. Li ⁺ /Li (45°C)	(0.2 C) 50th/85%, 200th/46%	Liquid phase coating	[85]
LiOH layer-NMC811	Li ₆ PS ₅ Cl	159.3 mAh·g ⁻¹ (0.1 C), 119.4 mAh·g ⁻¹ (1 C), 2.5–4.2V vs. Li ⁺ /Li (45°C)	(0.1 C) 500th/90%	Precursors for modulating cathode sintering	[95]
NCM811	Li ₃ InCl ₆	154 mAh·g ⁻¹ (0.1 C), 100 mAh·g ⁻¹ (2 C), 2.5–4.4 V vs. Li ⁺ /Li (25°C)	(0.1 C) 70th/97%	—	[23]
NCM88	Li ₃ YCl ₆	199 mAh·g ⁻¹ (0.1 C), 130 mAh·g ⁻¹ (4 C), 3.0–4.3V vs. Li ⁺ /Li (30°C)	(0.1 C) 200th/96.8%	Excessive amount of LYC (40.7wt%)	[35]

chemical properties in ASSLBs.

Walther *et al.* [85] investigated the effect of Li₂CO₃/LiNbO₃ coating on LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ on the decomposition of the positive side of Li₄Ti₅O₁₂/Li₆PS₅Cl/super C65 | Li₆PS₅Cl | NCM622/Li₆PS₅Cl/super C65 batteries. The authors synthesized a particle cladding layer with an average thickness of 15 nm and consisting of an amorphous LiNbO₃ core, a Li₂CO₃ shell, and a small amount of carbon-containing residue on the surface of NCM622 by liquid phase cladding with 300°C calcination. The Li₂CO₃/LiNbO₃ cladding layer was tested by EIS to reduce the interfacial impedance between the active substance and SSE. The results showed that the Li₂CO₃/LiNbO₃ coating successfully inhibited the interfacial reactions at the NCM/SSE interface and reduced the formation of byproducts such as phosphate and sulfate/

sulfite, as shown in Fig. 9(a) [85]. Zhang *et al.* [95] added the excess LiOH during NMC811 sintering and the spontaneous formation of a 10 nm-thick LiOH boundary capping layer as shown in Fig. 9(b). With its specific capacity of approximately 130 mAh·g⁻¹ and capacity retention of 90% for 600 cycles, the LiOH-coated NMC811 exhibits good cycling performance in Li₆PS₅Cl sulfide electrolytes. By comparing the electrochemical behavior at the interface of different cladding models through experiments and models, the authors finally concluded that the use of a LiOH coating layer that can completely cover NMC811 and has an appropriate thickness ensures the certain ionic conductivity and good electronic insulation of the interface layer and inhibits the decomposition of sulfide electrolytes. Deng *et al.* [24] devised an atomic layer deposition method to load lithium phosphate onto the lay-

er surface of NMC811 powder using lithium tert-butanol and trimethyl phosphate as precursors, followed by tempering at 600°C to allow LPO to enter the antiparticle grain boundaries of the secondary particles. As shown in Fig. 9(c), the capacity, cycle stability, and rate performance of the optimized hierarchical coverage LPO (HLPO)@NMC811 cathode are greatly increased. X-ray photoelectron spectroscopy (XPS)

and synchrotron X-ray absorption near edge structure (XANES) analysis showed that the LPO uniformly coated on the primary particle surface could effectively suppress the severe side reactions and surface structure evolution of bare NMC811 [24]. Surface doping and cladding during preparation endow good engineering applications for high-nickel layered cathodes.

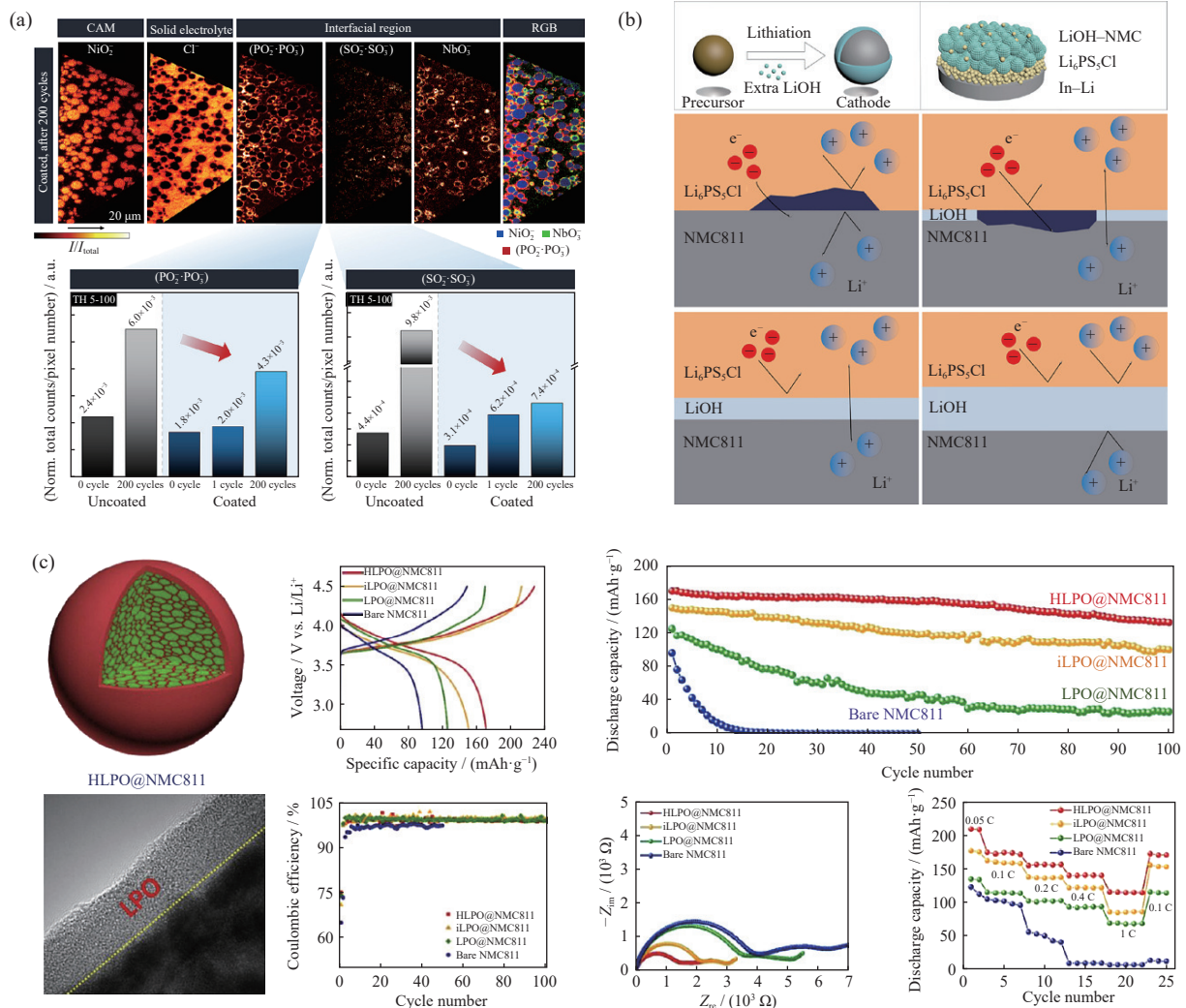


Fig. 9. (a) Time-of-flight secondary ion mass spectrometry (ToF-SIMS) images and results before and after the cycling of Li₂CO₃/LiNbO₃-coated NCM622 composite cathode. CAM and Norm. represent cathode active materials and signal strength normalization. (b) Schematic of NMC/Li₆PS₄Cl interface of the one-step coating process of LiOH-coated NMC811 and uncoated NMC811. (c) Schematic of high-nickel layered cathode cladding after dual-functional LPO modification in sulfide-based ASSLBs and comparison of electrochemical performance in different cladding states. iLPO represents infused LPO. (a) Reprinted with permission from F. Walther, F. Strauss, X.H. Wu, B. Mogwitz, J. Hertle, J. Sann, M. Rohnke, T. Brezesinski, and J. Janek, *Chem. Mater.*, vol. 33, 2110-2125 (2021) [85]. Copyright 2021 American Chemical Society. (b) Reprinted from *Energy Storage Mater.*, 41, Y.B. Zhang, X. Sun, D.X. Cao, G.H. Gao, Z.Z. Yang, H.L. Zhu, and Y. Wang, Self-stabilized LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ in thiophosphate-based all-solid-state batteries through extra LiOH, 505-514, Copyright 2021, with permission from Elsevier. (c) Reprinted from *Energy Storage Mater.*, 27, S.X. Deng, X. Li, Z.H. Ren, W.H. Li, J. Luo, J.W. Liang, J.N. Liang, M.N. Banis, M.S. Li, Y. Zhao, X.N. Li, C.H. Wang, Y.P. Sun, Q. Sun, R.Y. Li, Y.F. Hu, H. Huang, L. Zhang, S.G. Lu, J. Luo, and X.L. Sun, Dual-functional interfaces for highly stable Ni-rich layered cathodes in sulfide all-solid-state batteries, 117-123, Copyright 2020, with permission from Elsevier.

The interfacial reaction between the high-nickel layered cathode and the oxide layer can also be significantly reduced by the coating structure of the high-nickel layered cathode. Han *et al.* [96] used Li_{2.3}C_{0.7}B_{0.3}O₃ as an interfacial cladding material and found that it can slow down the interfacial reac-

tion between the active material and LATP oxide SSE during sintering, reduce the interfacial impedance of the ASSLB, and improve the capacity performance and cycling stability. This cladding layer for the high-nickel layered cathode can greatly slow down the interfacial reaction between the high-

nickel layered cathode and electrolyte, thus experimentally proving that this method can slow down the contact loss caused by the volume change of the high-nickel layered cathode itself. According to SEM characterization, the cladding structure allows the high-nickel layered cathode and SSE to remain in good contact after 50 cycles; by contrast, the bare high-nickel layered cathode shows severe cracking and loss of contact [91]. Halide SSEs have a high electrochemical window of thermodynamic stability at ≥ 4 V, and matched high-nickel layered cathodes can achieve good capacity performance without the need for coating treatment. Han *et al.* [35] matched NCM88 with LYC halide SSEs and achieved a capacity of $199 \text{ mAh}\cdot\text{g}^{-1}$ at a current density of 0.1 C and over 90% capacity retention after 200 cycles. Nevertheless, the interface between the halide SSEs and high-nickel layered cathode has not been clearly investigated, and the improvement options still need further research and validation. The construction of a buffer layer using the surface of high-nickel layered cathodes can prevent direct contact between the active material and electrolyte and slow down their interfacial reaction. One of the effective solutions is to use a suitable and protective layer that can slow down the interfacial contact loss by reducing the volume change of the high-nickel layered cathode during charging and discharging [91–96].

4. Conclusions and perspectives

Research progress in the use of high-nickel layered cathodes in inorganic solid electrolytes is reviewed from the aspects of electrochemical performance, interface problems, and optimization methods. The factors affecting the electrochemical performance of high-nickel layered cathodes in inorganic SSEs include inorganic SSE materials, particle structure and morphology of high-nickel layered cathodes, and composition and preparation methods of solid-state electrodes. The interface problems between these two materials involve the SCL effect, interfacial reaction, and mechanical contact loss, all of which affect the electrochemical performance, especially cycling. The clad SSE can effectively solve the electrochemical matching problem of the sulfide SSE and improve the stability of the polycrystalline high-nickel ternary material.

Owing to their good thermal and chemical stability, inorganic SSEs can significantly improve the safety of ASSLBs with high-nickel layered cathodes. Consequently, the electrochemical issues of high-nickel layered cathodes in inorganic SSEs are particularly critical. The use of high-nickel layered cathodes in vulcanization solid electrolytes endows good electrochemical stability, high specific capacity, and good cycle performance. A new type of inorganic SSE has been recently introduced in the electrochemical system with high-nickel layer cathodes, and this strategy shows a good development potential and has become an important research direction for ASSLBs. With their specific energy of more than 300 Wh/kg and intrinsically safe characteristics, ASSLBs with high-nickel layered cathodes are expected to achieve

technological breakthroughs in the near and medium terms and move toward the development stage of engineering and industrialization. For the developmental vision of ASSLBs with high-nickel layered cathodes, further research on the electrochemical properties and interfacial issues of high-nickel layered cathodes in SSEs must focus on the following: (1) The electrochemical system of high-nickel layered cathodes and inorganic SSEs must be further developed. On the one hand, inorganic SSEs with high electrochemical windows and high ionic conductivity, represented by new halide SSEs, must be developed. On the other hand, the surface coating of high-nickel layered cathodes must be optimized to build a stable interface between high-nickel layered cathodes and SSEs. (2) The basic science of the interface and electrode process between high-nickel layered cathodes and inorganic solid electrolytes must be clarified, the mechanism of the interface chemical reaction and electrochemical reaction between these two materials must be elucidated, and the intrinsic safety issues must be addressed. (3) The development of research and engineering technologies and preparation methods for high-nickel layered cathodes and solid electrolyte composite electrodes must be strengthened to promote the industrialization of ASSLBs.

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Conflict of Interest

The authors declared that they have no conflicts of interest to this work.

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