



Review Article

Coating materials and processes for cathodes in sulfide-based all solid-state batteries

Ayush Morchhale¹, Zhenghuan Tang¹, Chanyeop Yu², Rashid Farahati² and Jung-Hyun Kim¹**Abstract**

This short review focuses on critical issues related to the cathode/solid-electrolyte (SE) interface in all solid-state batteries (SSBs), including chemical instability, space-charge layer, and mechanical failure. Moreover, we reviewed recent R&D efforts to solve the issues by passivating the cathode interfaces using various materials (e.g. metallic oxides, carbonates, phosphates, halides, and polymers) and coating processes (e.g. sol-gel, dry coating, and atomic layer deposition). Finally, future perspectives have been outlined to understand fundamental electro-chemo-mechanical reactions occurring through coating layers to improve the performances of SSBs in the future.

Addresses

¹ Department of Mechanical and Aerospace Engineering, The Ohio State University, Columbus, OH 43210, USA

² Battery and Fuel Cell Development Group, Schaeffler Group USA Inc., Wooster, OH 44691, USA

Corresponding author: Kim, Jung-Hyun (kim.6776@osu.edu)

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Review, All solid-state batteries, Sulfide-based solid electrolyte, Cathode coating, Cathode, Solid electrolyte interface, Coating materials and processes.

Introduction

In the current era, researchers and industrialists have started working toward all solid-state batteries (SSBs) due to their high energy density, enhanced thermal safety, and stability [1,2]. Among all the categories of solid electrolytes (SEs), such as Li-stuffed garnet-phase oxides [3], perovskite [4], NASICON [5], lithium phosphorus oxynitride (LiPON) [6], and anti-perovskite [7], sulfide-based SEs have emerged as the prime candidate for SSBs due to their excellent ionic

conductivities (e.g. 2–25 mS/cm) that is comparable to conventional organic liquid electrolytes [8,9]. Additionally, sulfide-based SEs can offer good cycle life and high energy densities (>900 Wh/L) [10], which make them a front-runner in the manufacturing of light-weight, long-range, and safe SSBs for electric vehicles.

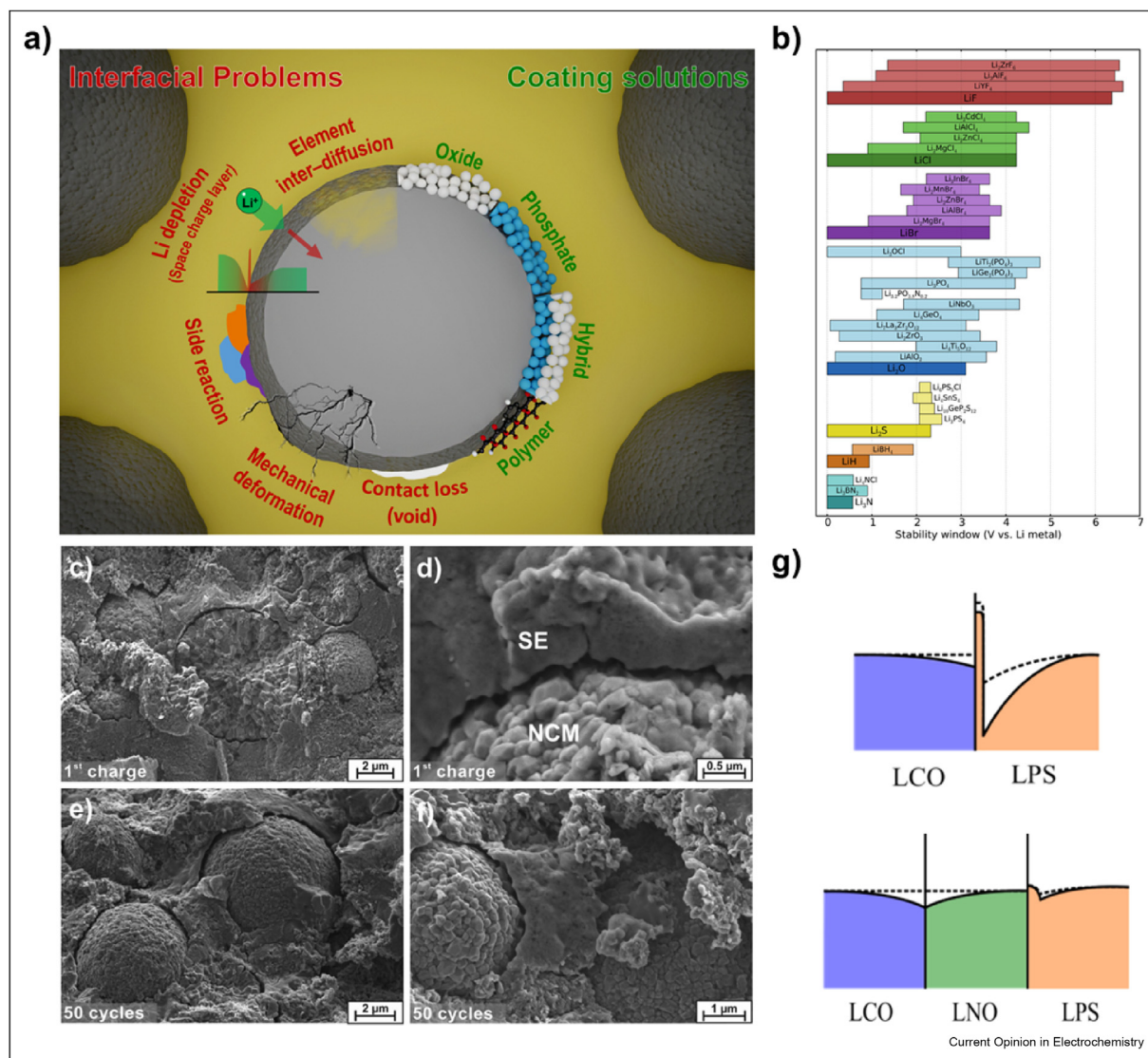
Despite the advantages, practical applications for Li-argyrodite SSB were still under-achieved due to a few technical challenges (Figure 1a). First of all, sulfide-based SEs have narrow electrochemical stability windows as shown in Figure 1b (e.g. 1.71–2.01 V for argyrodite [11]) which causes them to be thermodynamically unstable at both anode/SE [12] and cathode/SE interface [13–15]. Unwanted reaction products at the electrode-electrolyte interfaces increase cell impedance and degrade cell performance [16–19]. In addition, volumetric changes in cathode and anode during cycles cause the loss of interfacial contact and, therefore, increase interfacial resistances [20]. This electro-chemo-mechanical instability is a common issue for all different types of SSBs.

In this short review, we focus on the current state and progress on stabilizing the SE/cathode interface. The SE/cathode interface stability is one of the most critical issues of sulfide-based SSBs due to their electro-chemo-mechanical evolutions during cycling which is responsible for a premature cell death [21]. Techniques, such as coating passive materials on cathode, doping cathode materials, and synthesizing composite cathodes, have been successfully demonstrated for reducing parasitic reactions at the SE/cathode interface [19,22]. Among all the techniques, cathode coating stands out as it is a well-established process for manufacturing conventional Li-ion batteries. Here, we comprehensively described various problems at the interface between cathode and argyrodite SE and summarized different cathode-coating materials and processes that have been proposed in recent years. Finally, strategies for these interfacial problems and outlooks are prospected.

Electro-chemo-mechanical problems at SE/cathode

Various problems occurring at SE/cathode interface are responsible for SSB cell failure. We summarized the

Figure 1



(a) Schematic of cathode/SE interfacial problems and coating solutions by using different types of coating materials. (b) Electrochemical stability windows of various materials. Reprinted (adapted) with permission from [15]. Copyright 2016 American Chemical Society. Scanning electron microscopy images of NCM811 cathodes interfacing with β -Li₃PS₄ SE recorded (c,d) at first charge states, (e,f) after 50 cycles. Reprinted (adapted) with permission from [30]. Copyright 2017 American Chemical Society. (g) Elimination of space-charge layer by LiNbO₃ (LNO)-coated interlayer. Reprinted (adapted) with permission from [28]. Copyright 2014 American Chemical Society.

interfacial issues into the followings: chemical instability, space-charge layer, and mechanical failure [14,23,24]. First, the chemical side reaction of sulfide-based SE (both glass and crystal) stems from their very narrow electrochemical stability. For example, Mo et al. [11] suggested that the sulfur content in thio-phosphates tends to oxidize easily at 2.3 V_{vs.Li}. Since many common cathode materials have the nominal voltage above 3 V_{vs.Li} [11,25], sulfide-based SEs can be easily oxidized by bare cathode materials. As a result, Li-insulating layers, such as S, Li₂S_n, and P₂S_x, were produced at SE/cathode interface, which caused a large

capacity fading and interfacial impedance of SBBs during initial few cycles [26]. Also, surface-to-surface contact between cathode and SE leads to the interdiffusion of P element and transition-metal ions. The coefficient of diffusion and mutual solubility of mobile components affect the level of interdiffusion. The SEM image of contact loss between NCM811 and β -Li₃PS₄ SE after 1st and 50th cycle is shown in Figure 1c–f. At elevated temperature conditions during processing (synthesis) and cycling, accelerated interdiffusion of particles leads to the formation of interphase that hinders Li-ion transportation [24].

Additionally, the space-charge layer (Figure 1g) at the interface during early cycles was generally considered as one of the origins that hindered the Li-ion diffusion [27,28]. The interfacial gap in ionic conductivity and energy barrier results in the existence of space-charge layer during the transfer of Li-ions between cathode and electrolyte. The chemical potential difference between the cathode and Li-ion in sulfide SE develops an interfacial lithium-deficient layer. This results in the formation of mixed ionic and electronic conductive phases, thus, developing space-charge layer and lowering overall ion mobility and electrochemical stability [28]. Although the existence of the space-charge layer has been theoretically proven [29], its experimental existence still requires further understanding.

Finally, mechanical instability at the SE/cathode interface is one of the major reasons of the SSB performance degradation [30]. Most of conventional cathodes, such as LiCoO₂, LiNiO₂, and LiNi_xCo_yMn_zO₂ (NCM), experience volumetric changes (up to 8%) during lithiation/delithiation [31]. Even though sulfide-based SEs have relatively low Young's Modulus (~30 GPa), they can only accommodate extremely small elastic deformations, and such large volumetric changes cause loss in the contact and cracking at SE/cathode interface which, in turn, hinder the transportation of Li-ions and increase interfacial resistance [32].

Coating materials

Cathode coating has been widely accepted as one of the most promising ways to stabilize the SE/cathode interface. The important roles for coating are enhancing chemical stability and suppressing space-charge layers at the interface [11]. In this regard, the following property criteria will be considered when choosing a coating material: (i) high Li-ion conductivity, (ii) low electronic conductivity, and (iii) wide electrochemical stability window (Figure 1b). The coating layer needs to have good/moderate ionic conductivity for facile Li-ion transportation at the SE/cathode interface, which, in turn, suppresses the space-charge layer (Figure 1g) [28].

Since the unwanted oxidation reactions at SE/cathode interface originate from the electrochemical stability gap between cathode and SEs, the coating materials need to have a stability window wide enough to fill the gap [11,25]. At the same time, coating materials should retain electronically insulating property to serve as a kinetic barrier for electron hopping from SE to cathode.

Various coating materials have been employed to stabilize SE/cathode interface in sulfide-based SSBs. Table 1 listed the coating materials, properties, coating processes, cell configurations, and their performances reported in the literature. In this table, the coating materials have subgroups, such as oxides, phosphates, sulfides, polymers, and hybrids. Among them, metal

oxides [33–40] are the most popular due to their low cost and readiness to scale up. The oxides act as a physical barrier on SE/cathode interface, which can prevent the degradation of SE and improve the performances (e.g. capacity, cycle life, and rate capability). Among the coating materials, LiNbO₃ stands out as the most common coating material in recent research (Figure 2) due to its wide electrochemical stability window [25]. Nonetheless, its moderate ionic conductivity ($10^{-5} - 10^{-6}$ S/cm) requires thin coating layer (e.g. 1 wt% coating) as shown in Table 1. Also, Nb is not earth-abundant, and the use of flammable alcohol during wet-chemical coating process can be a safety concern when scaling up [36]. Therefore, recent R&D effort has been directed to searching alternative coating materials. For example, Li₂CO₃ is one promising candidate because of its lower cost and reasonable Li-ion conductivity (10^{-6} S/cm) [37]. Additionally, coating oxide-based SEs, such as Li_{0.35}La_{0.55}TiO₃, Li_{0.5}La_{0.5}TiO₃, and Li_{0.35}La_{0.5}Sr_{0.05}TiO₃, could facilitate the charge transfer reaction and hence improve the performance of cathodes in SSBs [41–43].

NASICON-type phosphate-based SEs, such as Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ (LATP) and Li_{1.5}Al_{0.5}Ge_{1.5}(PO₄)₃ (LAGP), have better anodic stabilities (e.g. stable up to 4.6 V_{vs,Li} for LATP and 4.9 V_{vs,Li} for LAGP) [44] than most oxides attribute to strong covalent bonding of polyanions. Combined with their good Li-ion conductivity (~ 10^{-4} S/cm in Table 1), phosphate-based SEs can stabilize the SE/cathode interface and improve the performance of SSBs [45].

There has been an approach to hybridize coating materials and tune the properties of SE/cathode interface. Kim *et al.* [37] adopted Li₂CO₃/LiNbO₃ as the hybrid coating onto cathode to obtain combined benefits from them; LiNbO₃ for preventing a release of harmful SO₂ and CO₂ gases and Li₂CO₃ for improving capacity retention and lower the material cost. The STEM image of LiNbO₃ and Li₂CO₃ hybrid coating is shown in Figure 2e–h. Similarly, Li₂CO₃ has been combined with Li₃BO₃ or Li₂ZrO₃ as the hybrid coating layers to further lower the material cost and enhance the performance [39,40].

Finally, polymers have been considered as alternative coating materials due to their good mechanical properties and manufacturability to form homogeneous coating layer with a good thickness control. The soft polymeric coatings can accommodate large volumetric changes of cathodes and suppress the delamination and cracking of the coating [48]. Since polyacrylonitrile may not have good Li-ion conductivity, Han *et al.* [49] used LATP + polyacrylonitrile composite as the hybrid coating on cathodes. In the composite, LATP offers a rapid Li-ion transportation while polyacrylonitrile passivates cathode surface uniformly.

Table 1

Summary of recent research on cathode coating materials in sulfide solid-state battery.

Category	Coating material	σ_f (S/cm)	Coating dimensions	Coating method	Cathode	Electrolyte	Anode	First discharge capacity (mAh/g)		Capacity loss per cycle (%)		Cycling conditions		Ref.	
								Bare	Coated	Bare	Coated	Voltage (V)	Current density		Temp. (°C)
Oxides	LiNiO ₃	10 ⁻⁵ –10 ⁻⁶	~2 nm/0.1 wt.%	Sol-gel and annealed (600 °C)	LiNi _{0.82} Mn _{0.06} Co _{0.12} O ₂	Li ₆ PS ₅ Cl	In-Li powder on Ni foil	141.1	147.6	1.72	1.07	1.9–3.9	34 mA/g	[38]	
			5–6 nm/1 wt.%	Sol-gel and annealed (400 °C)	LiNi _{0.9} Mn _{0.1} Co _{0.1} O ₂	Li ₁₀ GeP ₂ S ₁₂	In-Li	~162	~185	1.14	0.89	2.1–3.78	0.5 C	[33]	
			3 wt.%	Dry coated	LiNi _{0.9} Co _{0.2} Mn _{0.2} O ₂	Li ₇ P ₂ S ₆ J	Li _{0.5} In	127	135.1	4.02	0.78	2.38–3.68	15 mA/g	[51]	
			1 wt.%	Sol-gel and annealed (600 °C)	LiCoO ₂	Li ₁₀ GeP ₂ S ₁₂	In-Li	~110	~122	0.08	0.01	2.1–3.68	0.5 C	[53]	
			~5 nm/1 wt.%	Atomic layer deposition	LiNi _{0.9} Mn _{0.1} Co _{0.1} O ₂	Li ₆ PS ₄ Si _{1.5}	In	82.7	123.9	0.37	0.06	2.1–3.8	0.2 C	[54]	
			10.5 nm	Atomic layer deposition	LiNi _{0.9} Mn _{0.1} Co _{0.1} O ₂	Li ₁₀ SnP ₂ S ₁₂	Li ₄ Ti ₅ O ₁₂	~172	175	0.06	0.081	2.85–4.35	54 mA/g	[21]	
			<40 nm/0.1 wt.%	Sol-gel and annealed (400 °C)	LiCoO ₂	Li ₆ PS ₅ Cl	In-Li	112	142	0.22	0.15	3.0–4.5	0.2 C	[36]	
			~2 nm/0.1 wt.%	Sol-gel and annealed (600 °C)	LiNi _{0.82} Mn _{0.06} Co _{0.12} O ₂	Li ₆ PS ₅ Cl	In-Li powder on Ni foil	141.1	150.9	1.72	1.31	1.9–3.9	34 mA/g	[38]	
			3 wt.%	Dry coated	LiNi _{0.9} Co _{0.2} Mn _{0.2} O ₂	Li ₇ P ₂ S ₆ J	Li _{0.5} In	127	136.2	4.02	1.44	2.38–3.68	15 mA/g	[23]	
			2–4 nm/1 wt.%	Sol-gel	LiNi _{0.9} Co _{0.2} Mn _{0.2} O ₂	75Li ₂ S-22P ₂ S ₅ -3Li ₂ SO ₄	In-Li	124.4	146.3	0.83	0.56	1.88–3.88	17 mA/g	[61]	
			20 nm/2 wt.%	Sol-gel and annealed (350 °C)	LiCoO ₂	Li ₆ PS ₅ Cl	In-Li	94.5	142	0.40	0.07	2.2–3.6	0.1 C	[39]	
			1 wt.%	Sol-gel and annealed (600 °C)	LiNi _{0.9} Co _{0.15} Al _{0.05} O ₂	75Li ₂ S-22P ₂ S ₅ -3Li ₂ SO ₄	In-Li powder on Ni foil	113.6	143	0.22	0.36	1.88–3.88	17 mA/g	[62]	
			5 nm/0.5 mol%	Sol-gel and annealed (350 °C)	LiNi _{0.5} Co _{0.2} Mn _{0.3} O ₂	Li ₆ PS ₄	Graphite	107.1	146.5	0.57	0.22	2.5–4.3	0.05 mA/cm ²	[63]	
			2–4 nm/0.5 wt.%	Sol-gel and annealed (350 °C)	LiNi _{0.82} Co _{0.12} Mn _{0.06} O ₂	Li ₆ PS ₅ Cl	In-Li powder on Ni foil	175.4	194.1	0.66	0.28	1.9–3.7	0.5 C	[64]	
			5.2 nm/1 wt.%	Sol-gel and annealed (600 °C)	LiCoO ₂	Li ₆ Si _{1.74} P _{1.44} S _{11.7} Cl _{0.3}	In-Li	115.8	120	0.14	0.11	2.1–3.68	0.5 C	[34]	
		5.2 nm/1 wt.%	Sol-gel and annealed (600 °C)	LiCoO ₂	Li ₆ Si _{1.74} P _{1.44} S _{11.7} Cl _{0.3}	In-Li	115.8	128	0.14	0.06	2.1–3.68	0.5 C	[34]		
		20 nm	Sol-gel and annealed (150 & 400 °C)	LiNi _{0.5} Co _{0.3} Mn _{0.2} O ₂	Li ₆ PS ₅ Cl	In-Li	116	135	0.4	0.05	2.3–3.8	0.1 C	[41]		
		6 nm	Sol-gel and annealed (350 and 750 °C)	LiNi _{0.9} Co _{0.2} Mn _{0.2} O ₂	Li ₆ PS ₅ Cl	In-Li	143	179.9	0.57	0.15	2.2–3.7	0.1 C	[42]		
		15–20 nm	Sol-gel	LiNi _{0.33} Mn _{0.33} Co _{0.33} O ₂	Li ₆ PS ₅ Cl	In-Li	40	115	–	0.01	2.4–4	0.33 C	[43]		
		~10 nm/1 wt.%	Sol-gel and annealed (500 °C)	LiNi _{0.85} Mn _{0.05} Co _{0.10} O ₂	Li ₆ PS ₅ Cl	Li ₄ Ti ₅ O ₁₂	~142	~162	0.16	0.09	1.35–2.75	1 C	[65]		
		8–15 nm/1 mol.%	Sol-gel and annealed (750 °C)	LiNi _{0.33} Mn _{0.33} Co _{0.33} O ₂	Li ₆ PS ₄	Li ₄ Si	102	134	0.11	0.02	2.5–4.3	11 mA/g	[66]		
		<12 nm/1 wt.%	Dry coated and annealed (600 °C)	LiNi _{0.70} Mn _{0.15} Co _{0.15} O ₂	Li ₆ PS ₅ Cl	In-Li	~94	~122	0.8	0.46	2–3.7	0.25 C	[40]		
		2–3 nm	Atomic layer deposition and annealed	LiNi _{0.85} Co _{0.10} Mn _{0.05} O ₂	Li ₆ PS ₅ Cl	Li ₄ Ti ₅ O ₁₂	~95	~140	0.4	0.3	2.9–4.3	0.5 C	[67]		
Oxides															
	Al ₂ O ₃	~10 ⁻⁸													
	HfO ₂	–													
	TiO ₂	–													
	TiNb ₂ O ₇	–													
	ZrO ₂	–													
Carbonates															
	Li ₂ CO ₃	>10 ⁻⁶	max. 12 nm/1 wt.%	Sol-gel and annealed (300 °C)	LiNi _{0.9} Mn _{0.2} Co _{0.2} O ₂	β-Li ₃ PS ₄	Li ₄ Ti ₅ O ₁₂	106	124	0.36	0.21	1.35–2.85	0.1 C	[37]	
Phosphates															
	Li ₃ PO ₄	~10 ⁻⁷	5 nm	Atomic layer deposition	LiNi _{0.9} Mn _{0.1} Co _{0.1} O ₂	Li ₁₀ GeP ₂ S ₁₂	In	96.4	171	2	0.22	2.7–4.5	0.2 C	[69]	
	Li _{1.4} Al _{0.4} Th _{1.6} (PO ₄) ₃	9.5 × 10 ⁻³	8 nm		LiNi _{0.9} Co _{0.2} Mn _{0.2} O ₂	Li ₁₀ SnP ₂ S ₁₂	In-Li	~95	~146	0.60	0.12	2.1–3.9	0.1 C	[45]	

Hybrid	Li _{0.5} S _{0.4} F _{0.5} O ₄ LiNbO ₃ /doped LiCoO ₂	1.6 × 10 ⁻⁶	45 nm	Sol-gel and annealed (750 °C)	LiCoO ₂	80Li ₂ S-20P ₂ S ₅ Li ₁₀ GeP ₂ S ₁₂	In-Li	-90 -128	-80 -160	-	0.49	2.0-3.6 2.1-3.78	0.13 mA/cm ² 0.3 C	RT	[70] [46]
	Li ₂ CO ₃ /LiNbO ₃	>10 ⁻⁶	max. 12 nm/1 wt.%, 5-7 nm/1 wt.%, <40 nm/0.5 wt.%, <10 nm/1 wt.%, 10 nm/1 wt.%, 20 nm/0.5 wt.%, 5 nm	Sol-gel and annealed (400 °C)	LiNi _{0.8} Mn _{0.1} Co _{0.1} O ₂	β-Li ₆ PS ₄	Li ₄ Ti ₅ O ₁₂	106	136	0.36	0.09	1.35-2.85	0.1 C	25	[37]
	Li ₂ B ₂ O ₇ /LiNbO ₃	-	5-7 nm/1 wt.%, <40 nm/0.5 wt.%, <10 nm/1 wt.%, 10 nm/1 wt.%, 20 nm/0.5 wt.%, 5 nm	Sol-gel and annealed (300 °C)	LiNi _{0.8} Mn _{0.2} Co _{0.2} O ₂	Li ₆ PS ₅ Cl	Li	-51	-122	-0.67	-0.21	2.5-4.3	0.1 C	RT	[56]
	Li ₂ BO ₃ /Li ₂ CO ₃	6 × 10 ⁻⁷	<40 nm/0.5 wt.%, <10 nm/1 wt.%, 10 nm/1 wt.%, 20 nm/0.5 wt.%, 5 nm	Dry coated for Li ₂ B ₂ O ₇ and sol-gel for LiNbO ₃	LiNi _{0.8} Mn _{0.1} Co _{0.1} O ₂	Li ₆ PS ₅ Cl	In-Li	112	146	0.22	0.12	3.0-4.3	0.2 C	30	[36]
	Li ₂ CO ₃ /Li ₂ ZrO ₃	>10 ⁻⁶	<10 nm/1 wt.%, 10 nm/1 wt.%, 20 nm/0.5 wt.%, 5 nm	Sol-gel and annealed (600 °C)	LiCoO ₂	Li ₆ PS ₅ Cl	In-Li	162	170	0.71	0.54	1.35-2.85	0.2 C	45	[47]
	LiNbO ₃ /Li ₆ PS ₄	5.2 × 10 ⁻⁶	10 nm/1 wt.%, 20 nm/0.5 wt.%, 5 nm	Dry mixing - impact blending	LiNi _{0.8} Co _{0.2} Mn _{0.2} O ₂	Li ₆ PS ₄	Li ₄ Ti ₅ O ₁₂	-	-135	-	0.4	2.6-4.3	0.2 C	RT	[71]
	LiInO ₂ -LiI	-	20 nm/0.5 wt.%, 5 nm	Sol-gel	LiNi _{0.8} Co _{0.15} Al _{0.05} O ₂	75Li ₂ S-22P ₂ S ₅ -3Li ₂ SO ₄	In-Li	148.6	174.7	0.52	0.92	1.88-3.88	8.5 mA/g	30	[72]
	Poly(3,4-ethylenedioxythiophene)	-	5 nm	Molecular vapor deposition	LiNi _{0.8} Mn _{0.1} Co _{0.1} O ₂	Li ₁₀ GeP ₂ S ₁₂	In	-93	-190	0.86	0.48	2.1-3.8	0.1 C	RT	[73]
	Polyacrylonitrile	1.25 × 10 ⁻⁴ (σ _{electron}) ^a	3-5 nm/0.1%	Sol-gel and annealed (270 °C)	LiNi _{0.8} Mn _{0.1} Co _{0.1} O ₂	Li ₆ PS ₅ Cl	In	173.06	192.16	0.41	0.31	2.5-4.3	0.1 C	60	[48]
	Li _{1-x} Al _{0.4} Ti _{1.6} (PO ₄) ₃ and polyacrylonitrile	2.36 × 10 ⁻⁴ (σ _{electron}) ^a	1-2 nm	Sol-gel	LiNi _{0.8} Co _{0.2} Mn _{0.2} O ₂	Li ₁₀ GeP ₂ S ₁₂	In	-121	-125	0.08	0.05	2.8-4.3	0.5 C	25	[49]
	LiNbO ₃ and super C65	-	Both 1 wt.%, 4 nm	Sol-gel for LiNbO ₃ and dry mixing for super C65	LiNi _{0.8} Mn _{0.2} Co _{0.2} O ₂	Li ₆ PS ₅ Cl	Li ₄ Ti ₅ O ₁₂	163	173	-0.3	-0.3	1.35-2.85	0.1 C	25	[74]
	Diamond-like carbon	-	4 nm	Chemical vapor deposition	LiNi _{0.8} Co _{0.15} Al _{0.05} O ₂	75Li ₂ S-25P ₂ S ₅	Graphite	-90	-96	0.3	0.09	2.5-4	0.5 C	25	[75]

* RT: room temperature.

^a σ_{electron}: electronic conductivity value.

Coating processes

Various processes have been developed to provide uniform coatings on cathodes with a good thickness control and improve the SSB performances. At the same time, in practical perspectives, coating process should be cost-effective, less hazardous, and environmentally friendly. Atomic layer deposition (ALD) (Figure 3a) can precisely control the coating layer thickness (in angstrom scale), composition, crystallinity, and homogeneity. Such good coating quality helps in achieving high electrochemical performances compared with other coating techniques. For instance, LiNbO₃ coating on NMC cathode by ALD technique offered the most stable cycle life of SSB comparing with sol-gel and dry mixing methods in Table 1 [21,33,53,54,51]. Figure 2 compares LiNbO₃-coated layer produced by ALD, sol-gel, and dry coating methods. However, ALD process can increase the manufacturing cost and decrease commercial viability.

Wet chemical processes (Figure 3b), such as sol-gel and hydrothermal routes, have been used for commercial coating processes. Figure 2 shows that the sol-gel process can achieve good coating quality with homogeneous chemical compositions. Despite such promises, wet chemical processes may have safety concerns because they use flammable liquids during the process [36]. The waste liquid treatment and drying cathode material will add extra costs [55]. Further, cathode coating using the wet chemical processes can unwisely leach lithium from a cathode surface and degrade its performance [55].

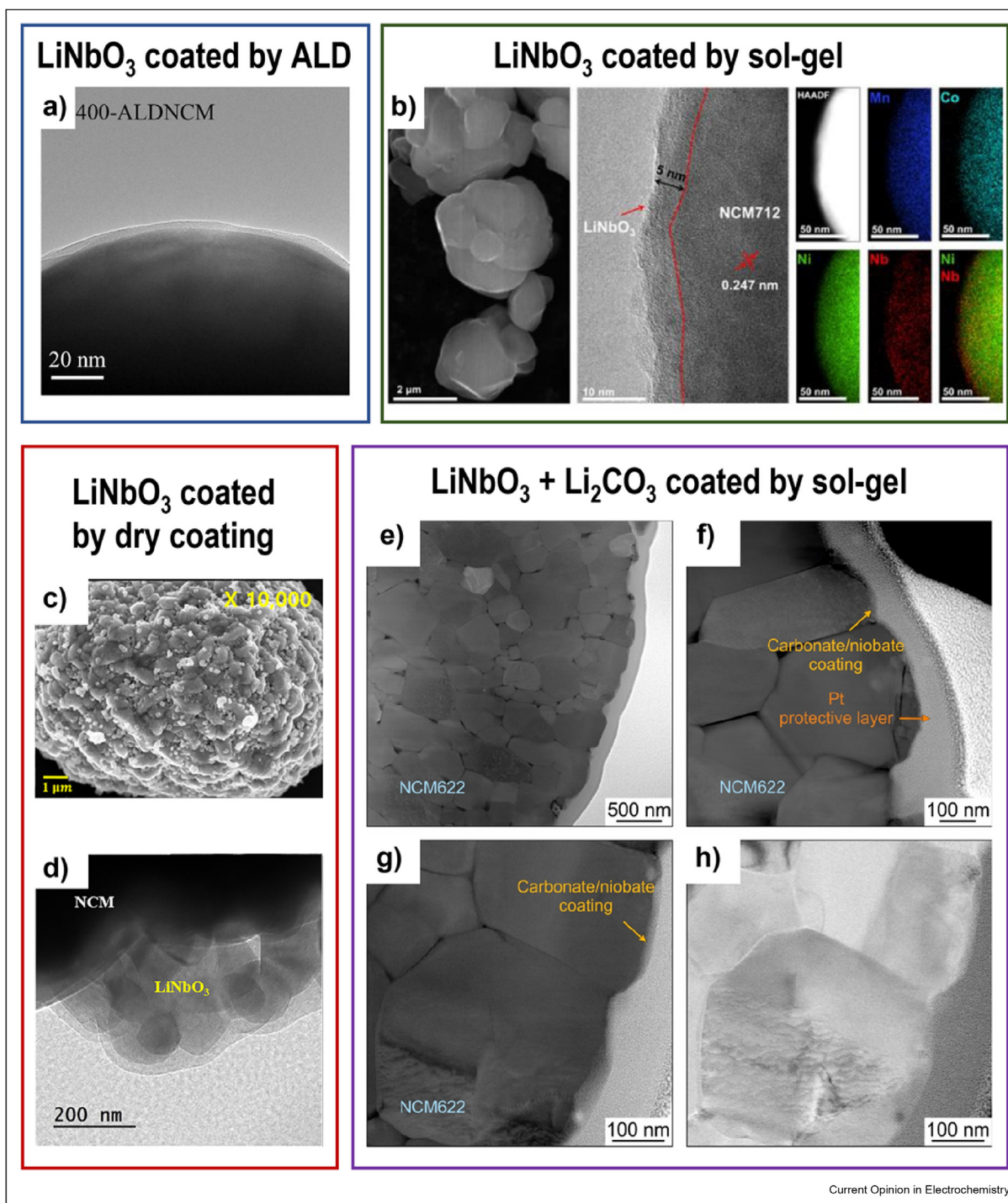
Dry coating process (Figure 3c) will be highly attractive in terms of scalability and cost-effectiveness. However, achieving good homogeneity and thickness uniformity via the dry coating will be more challenging than ALD or wet chemical coating processes. Thus, it will be essential to develop optimized processing conditions for the dry coating in practical applications. Earlier studies demonstrated that well-optimized dry ball milling can produce good quality coating and electrochemical performances [23,40,56].

Summary and future perspectives

Sulfide-based SSBs have been the most promising alternative to conventional liquid electrolyte-based Li-ion batteries. Nanoscale coating on cathode has been proven as a solution for passivating the SE/cathode and stabilizing SSB performances. In summary, we believe that the cathode coating layer needs to have the following properties: (1) moderate ionic conductivity (>10⁻⁶ S/cm), (2) low electronic conductivity (<10⁻¹² S/cm), (3) nanoscale thickness (<10 nm), and (4) wide electrochemical stability window at least covering from 1.7 V to 4.3 V_{vs,Li}. Also, the following points need to be addressed via future research.

1. Understanding the chemo-mechanical property evolution of the coated layers during the electrochemical

Figure 2

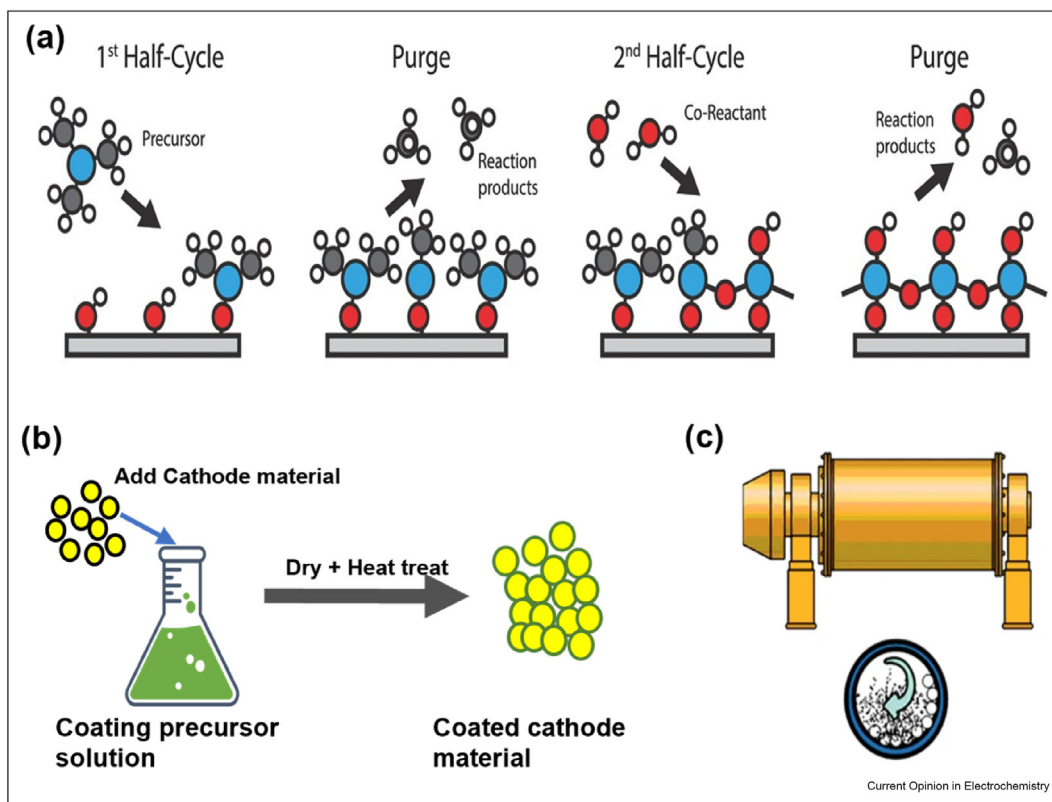


(a) SEM images of LiNbO₃-coated NCM by ALD method. Reprinted (adapted) with permission from [21]. Copyright 2021 American Chemical Society. (b) SEM/TEM/EDS images of LiNbO₃-coated NCM by sol-gel method. Reprinted (adapted) with permission from [50]. (c,d) LiNbO₃-coated NCM by dry coating method. Reprinted (adapted) with permission from [51]. (e–g) High-angle annular dark-field and (h) bright-field STEM images of LiNbO₃ + Li₂CO₃-coated NCM by sol-gel method. Reprinted (adapted) with permission from [52].

cycling: major R&D efforts have been focused on improving the chemical stability of SE/cathode at operating voltages of cathodes so far. However, there has been a lack of fundamental understanding about

the mechanical and chemical stability of the coating layers during long-term cycles of SSBs. *In situ* characterization techniques, such as *in situ* atomic force microscopy (AFM), *in situ* X-ray nano-CT, *in situ*

Figure 3



Schematics of different coating methods. (a) Atomic layer deposition (ALD). Reprinted (adapted) with permission from [57]. (b) Sol-gel method, and (c) dry ball milling. Reprinted (adapted) with permission from [58].

Raman, will be critical in answering the research questions. Recently reported polymer-inorganic hybrid-coating approach can broaden the scope of materials selection in terms of tuning the mechanical properties and extending the cycle life. We anticipated that computational modeling combined with experimental data can deepen the current understanding about the improvement mechanism of coating and offer a guidance for selecting the coating materials.

- Understanding the impact of carbon conductors on cathode/SE stability: in conventional Li-ion batteries, nano-sized carbon conductors (~ 50 nm) within cathode promote the oxidation of liquid electrolytes and degrade the interfaces at high voltages beyond the highest occupied molecular orbital (HOMO) of electrolytes. Recent studies showed the positive impact of adding small amounts of conductive carbon coating, such as diamond-like carbon and super C65 on the performance of SSBs. Although carbon conductors allow to build a good electronic conduction network, they facilitate electrochemical decomposition of the SE at cathode/SE interface and reduce cycle life [59,60]. Therefore, it will be necessary to develop coating strategies that can also passivate the carbon/SE interface in the future study.

- Explore the optimal coating process in terms of coating quality, cost, and scalability: we discussed three different coating methods: ALD, sol-gel, and dry coating. Currently, sol-gel is the most balanced way for coating process considering the interrelations among coating quality, cost, and scalability. However, it is still important to understand the quality and scalability of each coating method for the commercialization of SSBs in the future study.

CRedit author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could

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Data availability

No data was used for the research described in the article.

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* of special interest

** of outstanding interest

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