Supporting Information

복합 고체전해질과 고분자 바인더 기반 전고체전지 계면 및 공정 설계

김혜민[*], 진형준[*,,†]**

[*]인하대학교 고분자환경융합전공, [**]인하대학교 고분자공학과

Bridging Interfaces and Processing in All-Solid-State Batteries with Composite Solid Electrolytes and Polymer Binders

Hyemin Kim[*], and Hyoung-Joon Jin[*,,†]**

[*]*Program in Environmental and Polymer Engineering, Inha University, Incheon 22212, Korea*
[**]*Department of Polymer Science and Engineering, Inha University, Incheon 22212, Korea*

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[†]Corresponding Author:

E-mail: hjjin@inha.ac.kr

Tel: (+) 82-32-860-7483

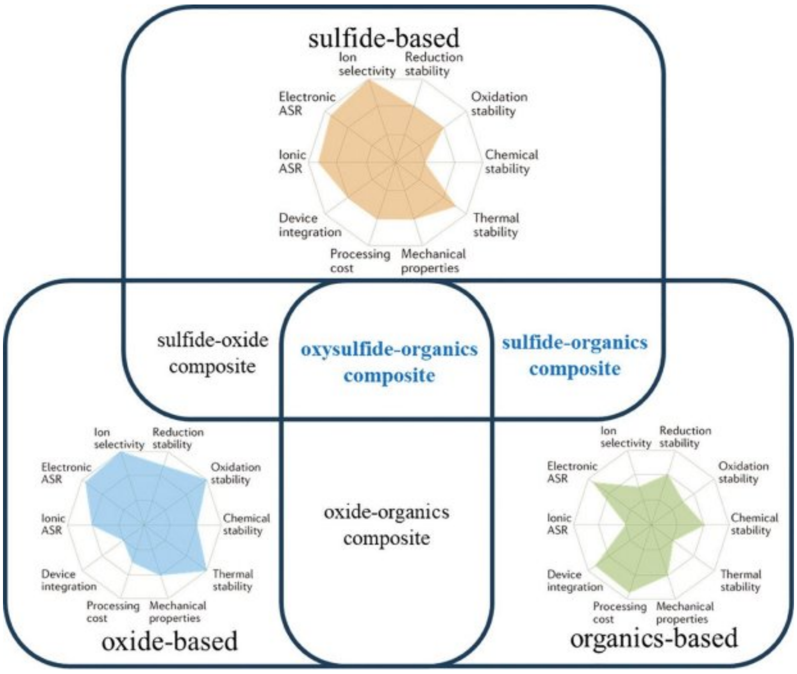

Figure S1. Radar plots of the performance properties and classification diagram for SSEs. ASR, area-specific resistance. ©*2024 Wiley-VCH GmbH* [1]

Table S1. Structural and Compositional Design Space of Composite Solid Electrolytes and Composite Cathodes

	Composite solid electrolyte (CSE)	Composite cathode (Active materials (AM)-Solid-state electrolyte (SSE)-C-binder)	Reference
Phases involved	Ceramic (sulfide/oxide/halide), polymer, Li salt, additives	Active material (Ni-rich NCM/NCA), SSE, conductive carbon, polymer binder	[19-24, 41-45]
Structural archetypes	Ceramic-continuous, polymer-continuous, dual/tri-continuous, core-shell, percolated networks	Random mixed composite, core-shell coated AM, half-shell, graded/gradient structures, infiltrated networks	[25-29, 58,59]
Main design targets	High Li^+ conductivity, wide electrochemical window, mechanical robustness, processability (film, pellet)	High areal capacity and electrode density, low composite and interfacial resistance, mechanical integrity under cycling	[34-36, 54-58]
Key compositional variables	Ceramic/polymer ratio, particle size and morphology, polymer type and crystallinity, Li salt type/concentration, fillers	AM:SSE:carbon:binder ratio (wt/vol), AM Ni content and particle structure, SSE type (sulfide/oxide/halide), carbon type, binder chemistry	[31-33, 50-53]
Processing routes	Slurry casting, in situ polymerization, hot pressing, dry mixing-compaction-roll-pressing/calendering	Slurry processing, dry-film processing, sequential mixing/coating, in situ polymerization in the porous cathode	[11, 37-40, 71, 81]
Interfacial focus	Ceramic-polymer interfaces, ceramic-ceramic grain boundaries, CSE-electrode interfaces	AM-SSE-carbon-binder triple junctions, AM/SSE and SSE/binder interfaces, interphase formation and stability	[12, 39, 40, 46-49]

Table S2. Representative Design Issues and Strategies at Ni-rich Cathode/solid Electrolyte Interfaces

Aspect	Sulfide SSE with Ni-rich cathode	Oxide SSE with Ni-rich cathode	Reference
Main interfacial issues	Oxidative decomposition of sulfide triggered by lattice oxygen release and high-valent Ni; formation of poorly conductive decomposition layers and accumulation of resistive interphases	High interfacial resistance due to poor physical contact and brittle fracture; possible reactions involving surface impurities such as Li_2CO_3/LiOH and cathode coating layers; stress accumulation at rigid-rigid contact	[61–65, 76–79]
Impact of high areal loading	Thicker cathodes amplify interfacial polarization and inhomogeneous current distribution; accumulation of interphase leads to rapid capacity fade	Thick cathodes exacerbate mechanical mismatch; cracking and delamination propagate from the interface into the bulk composite	[41-45, 56-59]
Chemical mitigation strategies	Cathode surface coatings (phosphate, oxyborate, oxyhalide, etc.), doped/modified sulfides, organic or polymer coatings on SSE	Cathode surface coatings ($LiNbO_3$, phosphates, fluorides), surface cleaning/conditioning of oxides, controlled co-sintering or sinter-free interface formation	[46-49,55]
Structural/ mechanical strategies	Optimized AM:SSE:carbon:binder ratio, fine sulfide dispersion, SPCSE and polymer interlayers as soft, ion-conducting buffer layers; dry-film densification with controlled porosity	Oxide/polymer composite interlayers, low-temperature lamination, polymer-in-ceramic skeletons providing mechanical cushion, tailored particle size and single-crystal Ni-rich cathodes	[39, 63–65]
Role of polymer	Ion-conducting binder/interlayer to reduce interfacial resistance, accommodate volume change, and homogenize Li^+ flux	Flexible buffer/interlayer improving contact and stress distribution, enabling sinter-free bonding and reduced cracking at high areal loading	[11, 71–73, 81]

Table S3. Target Specifications for Next-generation Polymer Binders in Practical All-solid-state Batteries

Dimension	For sulfide-based systems	For oxide-based systems	Reference
Function in the cell	Ion-conducting, mechanically robust binder for sulfide-based CSE and high-loading Ni-rich composite cathodes; optional interlayer at Li metal/SSE interface	Sinter-free adhesive and ion-conducting buffer for oxide CSE and Ni-rich cathodes; mechanical cushion and adhesive at oxide-electrode and Li/oxide interfaces	[12, 39, 40, 63–65, 80]
Ionic transport	Intrinsic Li^+ conductivity of polymer binder $\geq 10^{-5}$-10^{-4} S cm^{-1}; target composite conductivity of sulfide/binder phase $\geq 10^{-3}$ S cm^{-1}	Effective Li^+ conductivity in ceramic/polymer composite $\geq 10^{-4}$-10^{-3}S cm^{-1}	[19-24]
Mechanical properties	At 70-90 wt% sulfide: free-standing films (tens of µm), tensile strength ≥1 MPa, elongation of several tens of %, good recovery under cyclic compression	At 50–80 wt% ceramic: sufficient compressive modulus/strength to maintain ceramic–electrode contact, tensile strength in the MPa-to-tens-of-MPa range, and limited but non-brittle elongation to balance rigidity and toughness	[11, 56, 71, 72]
Processing window	Compatible with low-polarity/low-reactivity solvents or solvent-free in situ curing; curing/lamination ≤100-150 °C; suitable for slurry and dry-film processing	Enable room-temperature or ≤150 °C ceramic-ceramic and ceramic-electrode bonding (sinter-free); compatible with dry electrode and lamination processes	[57-59, 74]
Chemical / electrochemical stability	Oxidatively stable up to 4.3–4.5 V vs Li/Li^+ at the cathode side; reductively stable against Li metal when used as an anode-side interlayer; does not catalyze sulfide degradation or harmful gas evolution	High-voltage stability up to 4.5 V vs Li/Li^+; forms thin, ion-conductive interphases rather than thick insulating layers; interacts favorably with LLZO/NASICON surfaces and coatings	[34-36]
Interfacial anchoring	Mild but sufficient interactions with sulfide and cathode surfaces to ensure adhesion and stress buffering; can promote formation of beneficial SEI/CEI	Strong, selective anchoring to oxide surfaces/defects to suppress delamination and cracking; reduce ceramic-polymer interfacial resistance	[46-49]
Dry-process compatibility	Capable of fibrillation or 3D network formation during dry mixing-compaction-calendering; enables homogeneous mixing with sulfide powders	Forms robust 3D networks with ceramic particles in dry or low-solvent conditions; supports simultaneous forming of composite cathodes and solid electrolyte layers	[75–79]

References

Supporting Information에 사용된 참고문헌은 본문에 인용된 참고문헌과 동일함.