

Supplementary Information
Coating Layer Design Principles Considering Lithium Chemical Potential Distribution
within Solid Electrolytes of Solid-State Batteries

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Supplementary Note 1

Influence of the external current on the Li chemical potential (μ_{Li}) distribution

The influence of the external current on the μ_{Li} distribution is incorporated as the r parameter in the Eq. (12) in the main text, where $r < -1$ corresponds to charge and $r > 0$ corresponds to discharge conditions. Since solid-state batteries (SSBs) are not in a steady state during (dis)charging, the μ_{Li} distribution in SSBs under current flow cannot be accurately calculated using this equation; nevertheless, we employ this equation as a first approximation. Fig. S1 shows the μ_{Li} distribution under various charge or discharge currents. We assumed the cathode active material (CAM) loading in the cathode to be 20 mAh/cm^2 , which ranks among the highest values reported for SSBs¹. The σ_{ele} , σ_{Li^+} , and thickness of the coating layer (CL) are set to 1.0×10^{-14} , $1.0 \times 10^{-6} \text{ S/cm}$, and 10 nm , respectively, and the σ_{ele} , σ_{Li^+} , and thickness of the solid electrolyte (SE) are set at 1.0×10^{-11} , $0.5 \times 10^{-3} \text{ S/cm}$ and $100 \text{ }\mu\text{m}$, respectively, following the parameters used in the main text. Under charging currents, the μ_{Li} at the interface between the SE and CL escalates compared to that during the open circuit condition, with the increment being more pronounced for higher charging currents. Conversely, the μ_{Li} at the interface decreased as the discharging current increases. However, the μ_{Li} variation at the interface is limited to less than 0.2 eV , even under the (dis)charging current of 200 mA/cm^2 , which corresponds to 10C (dis)charge in SSBs that possess the highest CAM loading currently reported. Furthermore, as discussed in the main text, during (dis)charging of practical SSBs, the influence of the (dis)charging current is further diminished due to the electrode potential change accompanying (dis)charging and the electrode overpotential. Therefore, the influence of the external current on the thermodynamic stability of the interface can be regarded as relatively minor.

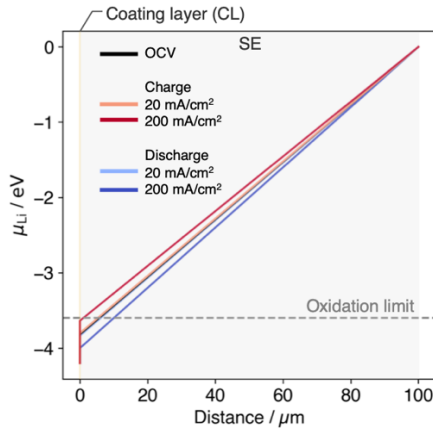


Fig.S1 μ_{Li} distribution under various (dis)charge currents. The CAM loading in the cathode is assumed to be 20 mAh/cm^2 . The σ_{ele} , σ_{Li^+} , and thickness of the CL are set to 1.0×10^{-14} , $1.0 \times 10^{-6} \text{ S/cm}$, and 10 nm , respectively, and the σ_{ele} , σ_{Li^+} , and thickness of the SE are set at 1.0×10^{-11} , $0.5 \times 10^{-3} \text{ S/cm}$ and $100 \text{ }\mu\text{m}$, respectively.

Supplementary Note 2

Calculation of the electron and ion conduction resistances of composite SSB electrodes using the two-dimensional (2D) lattice model

We assessed the electron and ion conduction resistances of composite SSB electrodes with CLs, employing a 2D lattice model of the composite electrode as depicted in Fig. 7b in the main text. The 2D lattice model was composed of 5 μm square lattices. There were 10 lattices in the thickness direction and 40 in the in-plane direction, with every lattice assigned to either the CAM or the SE. CL with a thickness of 10 nm was assigned to either all or a portion of the CAM or SE lattice surfaces. To perform calculations under these non-uniform thickness conditions, a mesh with progressively finer intervals approaching each lattice surface was assigned to the 2D lattice model. As boundary conditions, the electrostatic potentials at both ends of the model in the thickness direction were fixed at 0.1 and 0.0 V. Electric current across both ends of the model in the in-plane direction was assumed to be zero. The conductivity of the CAM, SE, or CL was assigned to each lattice, and the following Laplace's equation was solved using the conjugate gradient method to determine the electrostatic potential distribution within the 2D lattice model and the electric current values at both ends in the thickness direction,

$$\nabla \cdot (-\sigma \nabla \phi) = 0 \quad (\text{S1})$$

where ∇ , σ , and ϕ represent the divergence operator, conductivity, and electrostatic potential, respectively. We determined that the convergence was achieved when the difference in the electric current at both ends in the thickness direction reached 0.0001%. Then, the electron or ion conduction resistances of the 2D lattice model were calculated by dividing the voltage difference between the two ends by the absolute value of the electric current at convergence. When calculating the electron conduction resistance, the SE was assumed to be an electronic insulator, with only the CAM and CL contributing to the electronic conduction. Therefore, we assumed zero electric current flux into or out of each SE lattice. Conversely, when calculating the ion conduction resistance, the CAM was assumed to be an ionic insulator, with only the SE and CL contributing to the ionic conduction. Zero current flux was thus assumed into or out of each CAM lattice. The volume fractions of the CAM and SE were assumed to be 1:1. To exclude the influence of the configuration of the CAM and SE lattices, we statistically analyzed the resistances of 400 randomly generated configurations.

Supplementary Note 3

Description of the computational code to calculate the μ_{Li} distribution within the SE and CL

S3.1 General considerations and operating environment

The computational code is written in the Julia programming language and runs on Jupyter notebook. The code can be freely used and modified. However, when publishing results obtained using this code or its modified versions, please cite this paper (Y. Kimura *et al.*, "Coating Layer Design Principles Considering Lithium Chemical Potential Distribution within Solid Electrolytes of Solid-State Batteries", (2024)) appropriately. The authors are not responsible for any issues or problems caused by this code, its modifications, or the results generated by them. As the authors are not proficient in coding, please note that the code may contain complex or inefficient parts. The code has been confirmed to function correctly in the following operating environment (Supplementary Table S1), but its performance in other environments has not been verified.

Supplementary Table S1. Verified operating environment where the computational code has been confirmed to function properly.

Julia Version 1.7.2

Versions of the used packages other than the standard library:	Platform Info:
"CSV" => v"0.10.4"	OS: macOS (x86_64-apple-darwin19.5.0) CPU: Apple M2 Pro
"DataFrames" => v"1.3.4"	
"IJulia" => v"1.23.3"	
"Optim" => v"1.6.2"	
"PyPlot" => v"2.10.0"	

S3.2 Calculation model

In this computational code, the μ_{Li} distribution within the CL and SE of a one-dimensional SSB model with a cathode on the left and an anode on the right, as shown in Fig. S2, is calculated. Refer to this figure and set the input variables L , x_{int} , i_{ext} , E_{left} , and E_{right} accordingly. Then, set the ionic and electronic conductivities of the SE and CL. In this computational model, the ionic conductivity (σ_{ion}) is assumed to be constant, while the electronic defect conductivity (σ_{ele}) is assumed to be expressed by the following equation:

$$\sigma_{\text{ele}} = \sigma_{\text{e}}^0 (a_{\text{Li}})^{\text{expo}_{\text{e}}^0} + \sigma_{\text{h}}^0 (a_{\text{Li}})^{\text{expo}_{\text{h}}^0} \quad (\text{S2})$$

Here, σ_{e}^0 and σ_{h}^0 represent the conductivities of electrons and holes in the reference state, respectively. a_{Li} represents the Li activity, and expo_{e}^0 and expo_{h}^0 represent the exponents associated with a_{Li} . Assuming the defect equilibria commonly considered for Li defects, $\text{expo}_{\text{e}}^0 = 1$ and $\text{expo}_{\text{h}}^0 = -1$. If you wish to calculate the case where the conductivities of electrons and holes are independent of a_{Li} , set expo_{e}^0 and expo_{h}^0 to 0. The reference state is defined as the state where $a_{\text{Li}} = 1$. Note that this computational code may not function properly if the σ_{ele} values of the SE and CL differ too greatly. This model assumes a situation where a CL is inserted on the cathode side by default. However, by setting x_{int} to be significantly larger compared to $L - x_{\text{int}}$, the case where a CL is inserted on the anode side can also be calculated. In that case, input the values of the SE for $\sigma_{\text{ion_CL}}$, $\sigma_{\text{h_CL}}^0$, $\sigma_{\text{e_CL}}^0$, $\text{expo}_{\text{h_CL}}^0$, and $\text{expo}_{\text{e_CL}}^0$, and vice versa.

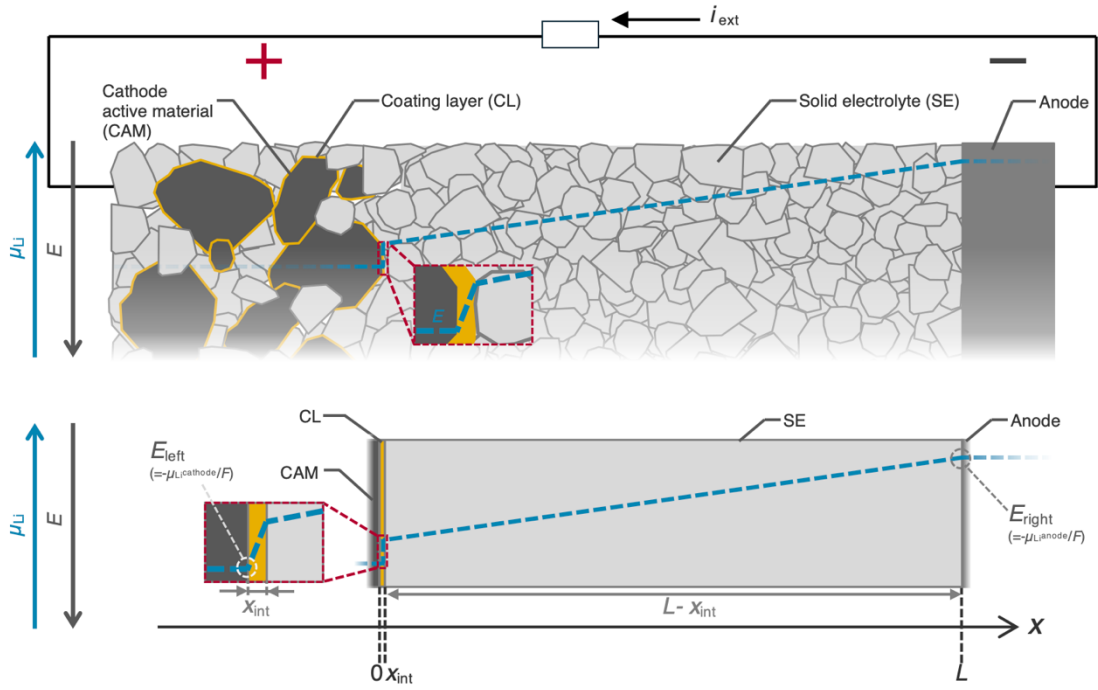


Fig.S2 One-dimensional SSB model assumed in the computational code.

References

1. Li, Y. *et al.* A lithium superionic conductor for millimeter-thick battery electrode. *Science* **381**, 50–53 (2023).