

# Quantifying the self-discharge rate of solid-state batteries

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## Supporting Information

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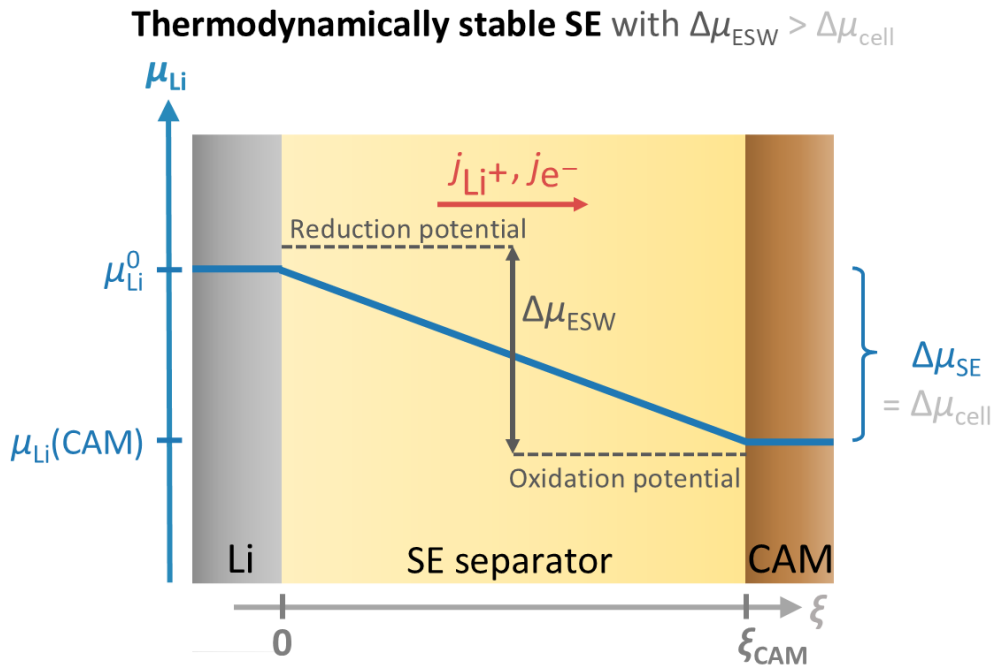
## Supplementary Note S1: The ISD Model for Different Solid Electrolyte Stability Cases

In general, three relevant cases of solid electrolyte stability and interface conditions must be distinguished for the ISD model:

- thermodynamically stable SEs at both interfaces with the negative and the positive electrode, *e.g.*,  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO),
- kinetically stable SEs with interphase formation at one or both electrode interfaces, and
- stabilized SEs with interfaces employing “artificial” protective interlayers (PILs), when interphase formation would otherwise severely compromise cell performance.

### Thermodynamically Stable Solid Electrolytes and Interfaces

**Fig. S1** represents the simplest case: a thermodynamically stable separator with no interphase formation, as the cell’s chemical potential difference (corresponding to the OCV) lies within the electrochemical stability window of the SE (*i.e.*,  $\Delta\mu_{\text{cell}} < \Delta\mu_{\text{ESW}}$ ).



**Figure S1: The lithium chemical potential profile  $\mu_{\text{Li}}$  (blue line) for a full-cell SSB employing a thermodynamically stable solid electrolyte.**  $\mu_{\text{Li}}$  of both the lithium metal negative electrode and the positive electrode (cathode active material, CAM) are within the separator’s electrochemical stability window ( $\Delta\mu_{\text{ESW}}$ ). Consequently,  $\mu_{\text{Li}}$  across the SE is confined within the cell’s chemical potential difference ( $\Delta\mu_{\text{cell}}$ ), that drives the coupled ISD fluxes for electronic ( $j_{e^-}$ ) and ionic ( $j_{\text{Li}^+}$ ) charge carriers. The depicted  $\mu_{\text{Li}}$  profile is schematic and does not necessarily follow a linear trend; it rather depends on the local transport properties of electrons (and holes) once a constant Li ion conductivity is assumed.

Here, the coupled molar flux of lithium (*i.e.*,  $j_{\text{Li}} \equiv j_{\text{Li}^+} = j_{\text{e}^-}$ ) across the separator (thickness  $\Delta\xi_{\text{SE}} = \xi_{\text{CAM}} - 0$ ) has to be considered to determine the internal self-discharge flux ( $j_{\text{SD}}$ ) upon integration of  $\nabla\mu_{\text{Li}}(\text{SE})$ .

$$\begin{aligned} j_{\text{Li}} &= -\overline{L_{\text{Li}}}(\text{SE}) \cdot \nabla\mu_{\text{Li}}(\text{SE}) = -\frac{\overline{L_{\text{Li}^+}(\text{SE}) \cdot L_{\text{e}^-}(\text{SE})}}{z_{\text{Li}^+}^2 \cdot \overline{L_{\text{Li}^+}(\text{SE})} + \overline{L_{\text{e}^-}(\text{SE})}} \cdot \frac{\mu_{\text{Li}}(\text{CAM}) - \mu_{\text{Li}}^0}{\xi_{\text{CAM}} - 0} \\ &= j_{\text{SD}} \cong -\overline{L_{\text{e}^-}}(\text{SE}) \cdot \frac{\Delta\mu_{\text{cell}}}{\Delta\xi_{\text{SE}}} \end{aligned} \quad (\text{eq. S1})$$

Here,  $\overline{L_i}$  are the average phenomenological transport coefficients,  $z_{\text{Li}^+} = 1$  is the charge number of lithium ions,  $\mu_{\text{Li}}$  is the chemical potential of lithium, and  $\Delta\mu_{\text{cell}} = \mu_{\text{Li}}(\text{CAM}) - \mu_{\text{Li}}^0$  is the cell's chemical potential difference.<sup>1</sup> Further notations (*e.g.*, spatial coordinate  $\xi_i$ ) follow the definitions in Fig. S1.

The partial conductivities are related to the transport coefficient by  $\sigma_i = (z_i \cdot F)^2 \cdot L_i$ . Assuming an ionic transference number close to unity with  $\overline{\sigma_{\text{Li}^+}} \gg \overline{\sigma_{\text{e}^-}}$ , eq. S1 can be reduced to:

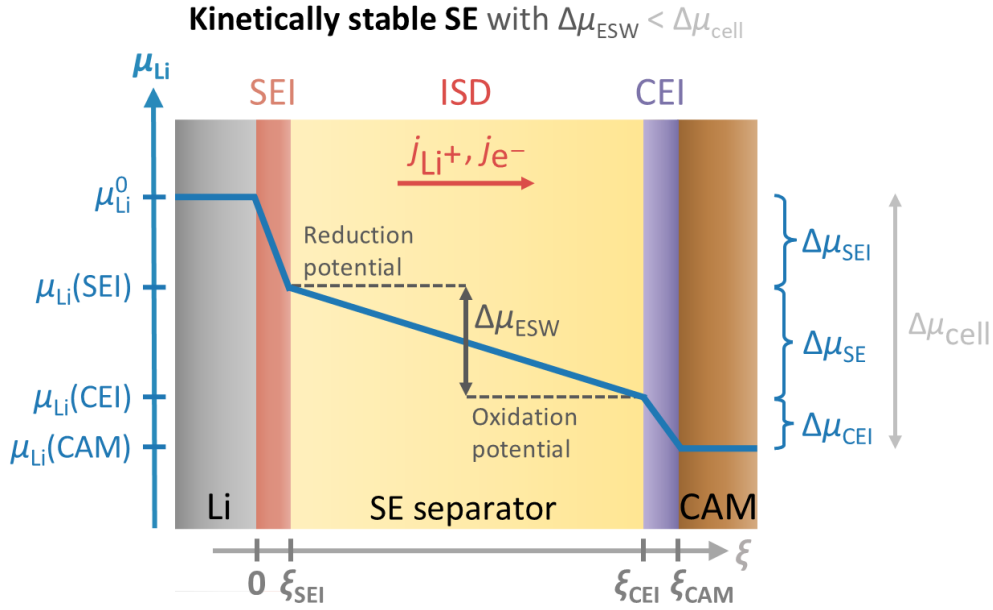
$$j_{\text{SD}} \approx \frac{1}{F^2} \cdot \overline{\sigma_{\text{e}^-}} \cdot \frac{F \cdot \Delta U_{\text{cell}}}{\Delta\xi_{\text{SE}}} = \frac{\overline{\sigma_{\text{e}^-}}}{F} \cdot \frac{\Delta U_{\text{cell}}}{\Delta\xi_{\text{SE}}} \quad (\text{eq. S2})$$

with  $\overline{\sigma_{\text{e}^-}}$  being the average partial conductivity of electronic charge carriers,  $F$  being the Faraday constant, and  $\Delta\mu_{\text{cell}} = -F \cdot \Delta U_{\text{cell}}$  relating the cell's open-circuit voltage ( $\Delta U_{\text{cell}}$ ) with the chemical potential difference of lithium across the separator.

Here, the internal  $j_{\text{SD}}$  is driven by the cell's potential difference  $\Delta\mu_{\text{cell}} = -F \cdot \Delta U_{\text{cell}}$  across the separator and governed by the average electronic conductivity ( $\overline{\sigma_{\text{e}^-}}$ ). The average electronic conductivity integrates the local conductivity along the separator and may include contributions from both electrons and electron holes, depending on the electronic structure of the SE. Eq. S2 essentially represents Ohm's law for electronic transport across the stable SE, driven by the OCV, as was also derived by Shao *et al.* and Deng *et al.*.<sup>2, 3</sup>

## Kinetically Stable Solid Electrolyte with Interphase Formation at One or Both Electrodes

This case corresponds to a SE (thermodynamically unstable against anode or cathode or both) that degrades chemically through reaction with the electrode(s), leading to interphase formation at one or both electrode interfaces. Here, interphase formation is kinetically limited. In the following, we focus on interphase formation at both electrodes (**Fig. S2**) for generality; analogous considerations apply when degradation occurs at only one interface.



**Figure S2: The lithium chemical potential profile  $\mu_{\text{Li}}$  (blue line) for a full-cell SSB employing a kinetically stable solid electrolyte.**  $\mu_{\text{Li}}$  of both the lithium metal negative electrode and the positive electrode (cathode active material, CAM) extend beyond the separator's electrochemical stability window ( $\Delta\mu_{\text{ESW}}$ ). Outside the ESW of the SE, SEI and CEI layers form at the negative and positive electrodes, respectively. Consequently,  $\mu_{\text{Li}}$  across the SE is confined within its stability range affecting the ISD fluxes for electronic ( $j_{e^-}$ ) and ionic ( $j_{\text{Li}^+}$ ) charge carriers. The depicted  $\mu_{\text{Li}}$  profile is schematic and does not necessarily follow a linear trend; it rather depends on the local transport properties of electrons once constant ionic conductivity is assumed in each region.

To account for interphase formation at both negative and positive electrodes (*i.e.*, SEI and CEI, respectively), the coupled molar fluxes of lithium (*i.e.*,  $j_{\text{Li}} \equiv j_{\text{Li}^+} = j_{e^-}$ ) across the interphase layers have to be considered:  $j_{\text{Li}}(\text{SEI})$ ,  $j_{\text{Li}}(\text{SE})$ , and  $j_{\text{Li}}(\text{CEI})$ . Similar to eq. S1, the individual fluxes can be expressed as:

$$j_{\text{Li}}(\text{SEI}) \cong -\overline{L_{e^-}}(\text{SEI}) \cdot \frac{\mu_{\text{Li}}(\text{SEI}) - \mu_{\text{Li}}^0}{\xi_{\text{SEI}} - 0} = -\overline{L_{e^-}}(\text{SEI}) \cdot \frac{\Delta\mu_{\text{SEI}}}{\Delta\xi_{\text{SEI}}} \quad (\text{eq. S3})$$

$$j_{\text{Li}}(\text{SE}) \cong -\overline{L_{e^-}}(\text{SE}) \cdot \frac{\mu_{\text{Li}}(\text{CEI}) - \mu_{\text{Li}}(\text{SEI})}{\xi_{\text{CEI}} - \xi_{\text{SEI}}} = -\overline{L_{e^-}}(\text{SE}) \cdot \frac{\Delta\mu_{\text{SE}}}{\Delta\xi_{\text{SE}}} \quad (\text{eq. S4})$$

$$j_{\text{Li}}(\text{CEI}) \cong -\overline{L_{e^-}}(\text{CEI}) \cdot \frac{\mu_{\text{Li}}(\text{CAM}) - \mu_{\text{Li}}(\text{CEI})}{\xi_{\text{CAM}} - \xi_{\text{CEI}}} = -\overline{L_{e^-}}(\text{CEI}) \cdot \frac{\Delta\mu_{\text{CEI}}}{\Delta\xi_{\text{CEI}}} \quad (\text{eq. S5})$$

Notations (*e.g.*, spatial coordinates  $\xi_i$ ) follow the definitions in Fig. S2. Analogous to the prior case (*i.e.*, a thermodynamically stable SE), the phenomenological transport coefficient could now be expressed in terms of partial conductivities as  $\sigma_i = (z_i \cdot F)^2 \cdot L_i$ . For simplicity, we do not pursue this here.

Given the layered arrangement and direction of fluxes, the internal self-discharge flux  $j_{\text{SD}}$  must be continuous (due to the conservation of charge). As all chemical potential differences are negative, all electron fluxes are positive, *i.e.*, directed “down-hill” toward the cathode:

$$j_{\text{SD}} = j_{\text{Li}}(\text{SEI}) = j_{\text{Li}}(\text{SE}) = j_{\text{Li}}(\text{CEI}) \quad (\text{eq. S6})$$

Rewriting eqs. S3-S5 in terms of the chemical potential differences across each layer gives:

$$\Delta\mu_{\text{SEI}} = \mu_{\text{Li}}(\text{SEI}) - \mu_{\text{Li}}^0 = -j_{\text{SD}} \cdot \frac{\Delta\xi_{\text{SEI}}}{\overline{L_{e^-}}(\text{SEI})} \quad (\text{eq. S7})$$

$$\Delta\mu_{\text{SE}} = \mu_{\text{Li}}(\text{CEI}) - \mu_{\text{Li}}(\text{SEI}) = -j_{\text{SD}} \cdot \frac{\Delta\xi_{\text{SE}}}{\overline{L_{e^-}}(\text{SE})} \quad (\text{eq. S8})$$

$$\Delta\mu_{\text{CEI}} = \mu_{\text{Li}}(\text{CAM}) - \mu_{\text{Li}}(\text{CEI}) = -j_{\text{SD}} \cdot \frac{\Delta\xi_{\text{CEI}}}{\overline{L_{e^-}}(\text{CEI})} \quad (\text{eq. S9})$$

with the chemical potential difference of lithium across the ESW of the SE being  $\Delta\mu_{\text{ESW}} = \Delta\mu_{\text{SE}} = \mu_{\text{Li}}(\text{CEI}) - \mu_{\text{Li}}(\text{SEI})$ . We consider this step particularly instructive. Eqs. S7 – S9 show that the chemical potential profiles along all three regions are controlled by their respective electronic transport properties. The lower the electronic conductivity of either SEI or CEI, the larger will be the chemical potential difference across SEI or CEI, leading to a lower chemical potential difference to which the SE bulk is exposed. Combining eqs. S7 and S9, yields the difference between the chemical potential drop across the full cell ( $\Delta\mu_{\text{cell}}$ ) and across the ESW ( $\Delta\mu_{\text{ESW}}$ ):

$$\begin{aligned} \Delta\mu_{\text{cell}} - \Delta\mu_{\text{ESW}} &= [\mu_{\text{Li}}(\text{CAM}) - \mu_{\text{Li}}^0] - [\mu_{\text{Li}}(\text{CEI}) - \mu_{\text{Li}}(\text{SEI})] \\ &= -j_{\text{SD}} \cdot \left[ \frac{\Delta\xi_{\text{CEI}}}{\overline{L_{e^-}}(\text{CEI})} + \frac{\Delta\xi_{\text{SEI}}}{\overline{L_{e^-}}(\text{SEI})} \right] \end{aligned} \quad (\text{eq. S10})$$

Clearly, the electronic properties of SEI and CEI play a major role for the ISD. Substituting eq. S8 for  $\Delta\mu_{\text{ESW}}$  yields:

$$\Delta\mu_{\text{cell}} = -j_{\text{SD}} \cdot \left[ \frac{\Delta\xi_{\text{CEI}}}{\overline{L_{e^-}}(\text{CEI})} + \frac{\Delta\xi_{\text{SE}}}{\overline{L_{e^-}}(\text{SE})} + \frac{\Delta\xi_{\text{SEI}}}{\overline{L_{e^-}}(\text{SEI})} \right] \quad (\text{eq. S11})$$

Eq. S11 states that the sum of the three ratios of layer thickness and electronic transport control the self-discharge. Defining the interphase thicknesses as a fraction of  $\Delta\xi_{\text{SE}}$ , *i.e.*, of the “core” separator thickness:  $\Delta\xi_{\text{SEI}} = f_{\text{SEI}} \cdot \Delta\xi_{\text{SE}}$  and  $\Delta\xi_{\text{CEI}} = f_{\text{CEI}} \cdot \Delta\xi_{\text{SE}}$ , with  $f_i$  being the respective scaling factor, yields:

$$j_{\text{SD}} = -\overline{L_{\text{e}^-}}(\text{SE}) \frac{\Delta\mu_{\text{cell}}}{\Delta\xi_{\text{SE}}} \cdot \frac{1}{\left[ \frac{f_{\text{CEI}} \cdot \overline{L_{\text{e}^-}}(\text{SE})}{\overline{L_{\text{e}^-}}(\text{CEI})} + 1 + \frac{f_{\text{SEI}} \cdot \overline{L_{\text{e}^-}}(\text{SE})}{\overline{L_{\text{e}^-}}(\text{SEI})} \right]} \quad (\text{eq. S12})$$

Using eqs. S8 and S11, the quotient  $\Delta\mu_{\text{ESW}}/\Delta\mu_{\text{cell}}$  can be derived (*i.e.*, how the cell voltage/potential difference is “buffered” by SEI and CEI):

$$\begin{aligned} \frac{\Delta\mu_{\text{ESW}}}{\Delta\mu_{\text{cell}}} &= \frac{\frac{\Delta\xi_{\text{SE}}}{\overline{L_{\text{e}^-}}(\text{SE})}}{\frac{\Delta\xi_{\text{SE}}}{\overline{L_{\text{e}^-}}(\text{SE})} \cdot \left[ \frac{f_{\text{CEI}} \cdot \overline{L_{\text{e}^-}}(\text{SE})}{\overline{L_{\text{e}^-}}(\text{CEI})} + 1 + \frac{f_{\text{SEI}} \cdot \overline{L_{\text{e}^-}}(\text{SE})}{\overline{L_{\text{e}^-}}(\text{SEI})} \right]} \\ &= \frac{1}{\left[ \frac{f_{\text{CEI}} \cdot \overline{L_{\text{e}^-}}(\text{SE})}{\overline{L_{\text{e}^-}}(\text{CEI})} + 1 + \frac{f_{\text{SEI}} \cdot \overline{L_{\text{e}^-}}(\text{SE})}{\overline{L_{\text{e}^-}}(\text{SEI})} \right]} \end{aligned} \quad (\text{eq. S13})$$

Lastly, substituting eq. S13 in eq. S12 yields the final expression:

$$\begin{aligned} j_{\text{SD}} &= -\overline{L_{\text{e}^-}}(\text{SE}) \frac{\Delta\mu_{\text{cell}}}{\Delta\xi_{\text{SE}}} \cdot \frac{\Delta\mu_{\text{ESW}}}{\Delta\mu_{\text{cell}}} \\ &= -\overline{L_{\text{e}^-}}(\text{SE}) \frac{\Delta\mu_{\text{ESW}}}{\Delta\xi_{\text{SE}}} \end{aligned} \quad (\text{eq. S14})$$

Here, the internal  $j_{\text{SD}}$  is governed by the SE’s ESW, with  $\Delta\mu_{\text{ESW}} = -F \cdot \Delta U_{\text{ESW}}$  across the separator confined between  $\mu_{\text{Li}}(\text{SEI})$  and  $\mu_{\text{Li}}(\text{CEI})$ . Consequently,  $\Delta\mu_{\text{ESW}}$  is defined by the standard free energy change ( $\Delta_r G$ ) during the decomposition of the corresponding SE, divided by the stoichiometric factor ( $x_{\text{Li}}$ ) of the decomposition reaction:  $\Delta\mu_{\text{ESW}} = \Delta_r G / x_{\text{Li}}$ . Thus, by charge conservation, the SEI and CEI grow until the electronic flux across all three layers in series (*i.e.*, SEI, SE bulk, and CEI) becomes equal in the quasi-stationary state. At this point, it is sufficient to consider only the SE bulk and its electronic transport properties (*i.e.*,  $\overline{L_{\text{e}^-}}$ ), as the effects of the SEI and CEI are implicitly contained (eq. S14).

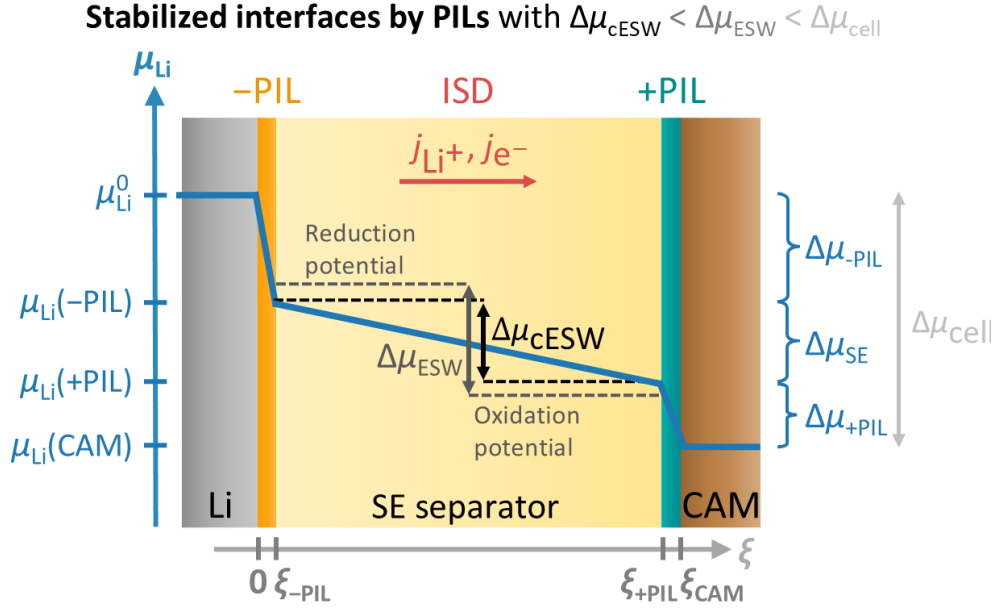
Here, eq. S12 can also be used to estimate the impact of interphases on the internal  $j_{\text{SD}}$ . Assuming interphases are 1000x thinner than the SE (*i.e.*,  $f_{\text{SEI}} = f_{\text{CEI}} = 0.001$ ) and that the electronic conductivity of the SE is higher than the electronic conductivity of the SEI and CEI (*i.e.*,  $\overline{L_{\text{e}^-}}(\text{SE}) = 100 \cdot \overline{L_{\text{e}^-}}(\text{SEI}) = 100 \cdot \overline{L_{\text{e}^-}}(\text{CEI})$ ), we obtain:

$$j_{\text{SD}} = -\overline{L_{\text{e}^-}}(\text{SE}) \frac{\Delta\mu_{\text{cell}}}{\Delta\xi_{\text{SE}}} \cdot \frac{1}{\left[\frac{f_{\text{CEI}}}{0.01} + 1 + \frac{f_{\text{SEI}}}{0.01}\right]} = -\overline{L_{\text{e}^-}}(\text{SE}) \frac{\Delta\mu_{\text{cell}}}{\Delta\xi_{\text{SE}}} \cdot \frac{1}{1.2} \quad (\text{eq. S15})$$

Thus,  $j_{\text{SD}}$  (*i.e.*, its driving force) is reduced by  $\sim 17\%$  for these assumptions.

## Stabilized Solid Electrolyte with Interfaces Employing “Artificial” Protective Interlayers

If native interphases are insufficient to suppress ISD or significantly increase the cell’s ionic resistance, “artificial” protective interlayers (PILs) are often explored to stabilize SE degradation at the electrode interfaces. This scenario is considered in **Fig. S3** with PILs at both electrode interfaces. Here, we consider fully covering PILs of high quality and homogeneity with sufficiently high ionic conductivity and presumably low  $\overline{L}_{e^-}$  and  $\overline{\sigma}_{e^-}$ .



**Figure S3: The lithium chemical potential profile  $\mu_{\text{Li}}$  (blue line) for a full-cell SSB employing protective interlayers at both electrode interfaces to stabilize the solid electrolyte.**  $\mu_{\text{Li}}$  is shifted by the PILs at both the negative and positive electrodes within the separator’s electrochemical stability window ( $\Delta\mu_{\text{ESW}}$ ). Consequently,  $\mu_{\text{Li}}$  across the SE is confined within the “controlled” ESW ( $\Delta\mu_{\text{cESW}}$ ) affecting the ISD fluxes for electronic ( $j_{e^-}$ ) and ionic ( $j_{\text{Li}^+}$ ) charge carriers. The depicted  $\mu_{\text{Li}}$  profile is schematic and does not necessarily follow a linear trend; it rather depends on the local transport properties of electrons.

Analogous to both prior cases, the internal  $j_{\text{SD}}$  for stabilized and protected interfaces is now governed by the “controlled ESW” with  $\Delta\mu_{\text{ESW}} > \Delta\mu_{\text{cESW}} = -F \cdot \Delta U_{\text{cESW}}$  across the SE thickness (*i.e.*,  $\Delta\xi_{\text{SE}} = \xi_{+\text{PIL}} - \xi_{-\text{PIL}}$ ). Here,  $\Delta\mu_{\text{cESW}}$  is confined between  $\mu_{\text{Li}}$  of the negative PIL and positive PIL (*i.e.*,  $-\text{PIL}$  and  $+\text{PIL}$ ), respectively, and can be tuned through the choice of interlayer materials.<sup>4, 5</sup>

$$j_{\text{SD}} = -\overline{L}_{e^-}(\text{SE}) \frac{\Delta\mu_{\text{cESW}}}{\Delta\xi_{\text{SE}}} \quad (\text{eq. S16})$$

Ideally, both PILs should be fully covering yet very thin, with high ionic and low electronic partial conductivity, so as to minimize their ionic resistance while suppressing ISD and inter-phase formation by appropriately shifting  $\Delta\mu_{\text{Li}}$  within the ESW.

### Supplementary References

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