

# A Diffuse-Interface Model for Predicting the Evolution of Metallic Negative Electrodes and Interfacial Voids in Solid-State Batteries with

S Chatterjee

September 2025

Journal of the Electrochemical Society

## **Disclaimer**

---

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

# A diffuse-interface model for predicting the evolution of metallic negative electrodes and interfacial voids in solid-state batteries with homogeneous and polycrystalline solid electrolyte separators.

Sourav Chatterjee<sup>a,b,\*\*</sup>, Michael Tonks<sup>a,\*\*</sup>, William Gardner<sup>c</sup>, Marina Sessim<sup>c</sup>

<sup>a</sup>Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611, USA

<sup>b</sup>Materials Science Division, Lawrence Livermore National Laboratory, Livermore, CA 94550, USA

<sup>c</sup>QuantumScape Battery, Inc., 1730 Technology Drive, San Jose, CA 95110, USA

---

## Abstract

This paper presents a novel diffuse-interface electrochemical model that simultaneously simulates the evolution of the metallic negative electrode and interfacial voids during the stripping and plating processes in solid-state batteries. The utility and validity of this model are demonstrated for the first time on a cell with a sodium (Na) negative electrode and a Na- $\beta''$ -alumina ceramic solid electrolyte (SE) separator. Three examples are simulated. First, stripping and plating with a perfect electrode/electrolyte interface; second, stripping and plating with a single interfacial void at the electrode/electrolyte interface; third, stripping with multiple interfacial voids. Both homogeneous SE properties and polycrystalline SEs with either low or high conductivity grain boundaries (GBs) are considered for all three examples. **Heterogeneous GB conductivity marginally impacts the thickness of the Na electrode in cases with a perfect electrode/electrolyte interface. Moreover, it results in local changes to void growth due to the interactions between the void edge and the GBs.** The void growth rate is a linear function of the flux of Na atoms at the void edge, which in turn depends on the applied current density. We also show that the void coalescence rate increases with applied current density and can be marginally influenced by GB conductivity.

**Keywords:** Batteries, Electrodeposition - modeling, Interfacial voids, Theory and Modelling

---

## 1. Introduction

Since the 1990s, lithium (Li)-ion batteries (LIBs) have been the prevalent form of energy-storage technology used in portable devices and electric vehicles [1, 2]. However, conventional LIBs with a

---

\*Sourav Chatterjee

\*\*Michael Tonks

Email addresses: chatterjee5@llnl.gov (Sourav Chatterjee), michael.tonks@ufl.edu (Michael Tonks), WGardner@quantumscape.com (William Gardner), MSessim@quantumscape.com (Marina Sessim)

graphite negative electrode are soon expected to reach their specific energy limit ( $\sim 250$  Wh/kg) [3–5]. By replacing graphite with Li metal as the negative electrode, cells with higher specific energy ( $> 500$  Wh/Kg) and voltage could be potentially realized because Li has  $\sim 10$  times higher specific capacity (3861 mAh/g) than graphite (372 mAh/g); and has one of the lowest standard reduction potentials ( $-3.04$  V vs standard hydrogen electrode) [5–7]. However, the global reserves of Li are limited, and the future cost of Li is expected to increase given the rising energy-storage demands [8, 9]. Batteries with metallic sodium (Na) negative electrodes are an attractive alternative to Li metal batteries because Na is more abundant and has a lower cost than Li and has a higher specific capacity (1166 mAh/g) than graphite.

Batteries with metallic negative electrodes and ionically-conducting liquid electrolytes fail due to dendrite-induced cell shortcircuiting [7, 10–12]. Another disadvantage of liquid electrolytes is that they are highly flammable [1]. Substituting liquid electrolytes with ionically-conducting ceramic-based solid electrolytes is a promising strategy to enable metallic negative electrodes and mitigate the fire risk associated with LIBs. Consequently, all-solid-state batteries (ASSBs) with metallic negative electrodes and ceramic-based solid-state electrolytes are considered a safer and promising alternative to LIBs [13].

Despite these advantages, ASSBs can fail due to void-induced dendrite formation at relatively high cycling current densities [14, 15], making them unsuitable for fast-charging applications. Several researchers have reported Na or Li dendrite penetration through the ceramic-based solid electrolyte separators at cycling current densities that are well below the desired current densities required for fast-charging applications [16–21] [22] [11], [23]. Recently, Kasemchainan *et al.* [19] pointed out two critical current densities that are relevant in understanding dendrite formation during the cycling of ASSBs. First is the critical current density for plating (CCP), above which cell failure invariably occurs due to dendrite formation. Second is the critical current density for stripping (CCS), above which cell failure occurs due to void-induced dendrite formation. Cycling above CCS inevitably leads to void formation at the electrode/solid electrolyte separator interface. These voids increase the interfacial resistance [24] and cause the current to get concentrated near the void edges. During subsequent charging cycle, these current density hotspots induce dendrite formation as the local current density may well exceed CCP [19], [21] [25–27]. Consequently, the CCS determines the maximum cycling current density below which ASSBs can be safely cycled without dendrite formation [28]. Thus, understanding factors that mitigate void formation and increase CCS can help design practical and fast-charging ASSBs.

Several experimental groups [14, 15, 28–31], including Kasemchainan *et al.* [19], have suggested



factors that enhance CCS in ASSBs with metallic electrodes. One is applying an increased stack pressure on the metallic negative electrode as it suppresses void growth due to creep deformation. Another factor that helps reduce void formation is using alkali metal electrodes with lower creep resistance, such as Na or potassium [32]. This explains why Na-metal ASSBs typically exhibit higher CCS than Li-metal ASSBs for a given applied stack pressure and temperature [15]. For instance, Jolly *et al.* [28] reported CCS to be around  $1.5 - 2.5 \text{ mA/cm}^2$  at room temperature in an ASSB with a Na negative electrode and a Na- $\beta''$ -alumina ceramic solid electrolyte separator when cycled under a stack pressure of  $4 - 9 \text{ MPa}$ . Although these factors are useful indicators in mitigating void growth, a quantitative understanding of the impact of metallic electrodes and solid electrolyte properties on void evolution is still lacking.

Moreover, atomistic [33, 34] and continuum scale [35–37] models have been proposed in the literature to understand void formation and growth in ASSBs. However, these works have been applied only to Li metal batteries. For instance, Yang *et al.* studied the impact of adhesion energy and pressure on void formation in a Li-metal/ $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) cell using large-scale molecular dynamics simulations. Their results suggest strong interface adhesion and high pressure mitigate void formation during stripping [33]. At the continuum scale, Zhao *et al.* [36] used the phase-field method to simulate the evolution of micron-sized single and multiple interfacial voids in a Li/LLZO cell. Consistent with experimental observation [19], they showed that an interfacial void grows during stripping and shrinks during plating preferentially along the electrode/solid electrolyte interface. Agier *et al.* [35] used a sharp-interface approach to show that sufficient Li flux concentration is required for void growth to occur during stripping in a Li/LLZO cell. Barai *et al.* [37] showed the impact of both bulk and surface diffusion of Li on void growth in a Li/LLZO cell. One limitation of these works is that they all assume a homogenous solid electrolyte separator. Typical solid electrolyte separators in ASSBs are polycrystalline, consisting of grain boundaries (GBs) with an ionic conductivity higher or lower than the grain interior [38–41]. These GBs are believed to provide paths for dendrite propagation in ASSBs [16, 42, 43]. Thus, quantifying the impact of GB transport properties on interfacial void evolution is essential.

Another aspect missing from these continuum-scale models is the shrinkage and expansion of the negative electrode that occurs during the stripping and plating of an ASSB. The thickness of the electrode changes because of the movement of the electrode/electrolyte interface at a rate proportional to the interfacial current density [44]. Capturing the movement of the electrode/electrolyte interface while

simultaneously considering the inhomogeneities at this moving interface is numerically challenging. To overcome this issue, Narayan and Anand [45] proposed a mechanics-based model that simulates the shrinkage and growth of the negative electrode using a hypothetical interphase layer between the Li metal and the LLZO solid electrolyte with a perfect interface with no voids. Alternatively, Jang *et al.* [46, 47] introduced a phase-field model similar to immersed-interface approaches to simulate the evolution of Li negative electrode with a liquid electrolyte by explicitly considering the moving sharp interface condition at the electrode/electrolyte interface. Since they model a liquid electrolyte, their approach assumes that the electrode/electrolyte interface remains perfect during stripping and plating.

This work presents a novel phase-field model that can simultaneously simulate the evolution of metallic negative electrodes and interfacial voids in an ASSB. Furthermore, we consider homogenous and polycrystalline solid electrolytes with low-conductive and high-conductive GBs. Although phase-field models considering solid-electrolyte GB properties exist in the literature [42], these models neither consider the evolution of interfacial voids nor that of the negative electrode. Moreover, contrary to previous works, we apply our model to an all-solid-state cell with a Na negative electrode and Na- $\beta''$ -alumina ceramic solid electrolyte separator. To the best of our knowledge, stripping and plating of a Na metal solid-state cell has never been simulated. Our goal in this work is twofold. First, to model the shrinkage and growth of the metallic negative electrode during stripping and plating under an applied current density, assuming a perfect electrode/electrolyte interface. Second, to model the evolution of interfacial voids while simultaneously considering the volume change occurring in the negative electrode. In addition, we report on the impact of solid electrolyte GBs on the evolution of the metallic negative electrode and interfacial voids.

This paper is organized as follows. In Section 2, we formulate a multi-phase-field model and provide the governing equations with the interfacial and boundary conditions. In Section 3, we parameterize the model to simulate a cell with a Na negative electrode and a Na- $\beta''$ -alumina solid electrolyte separator. In Section 4, we use three test cases in each subsection to demonstrate the utility and validity of our model. These subsections are subdivided into a homogeneous solid electrolyte case and polycrystalline solid electrolyte cases with low-conductive and high-conductive GBs. In Section 5, we finish with some concluding remarks and indicate possible future directions.

## 2. Formulation

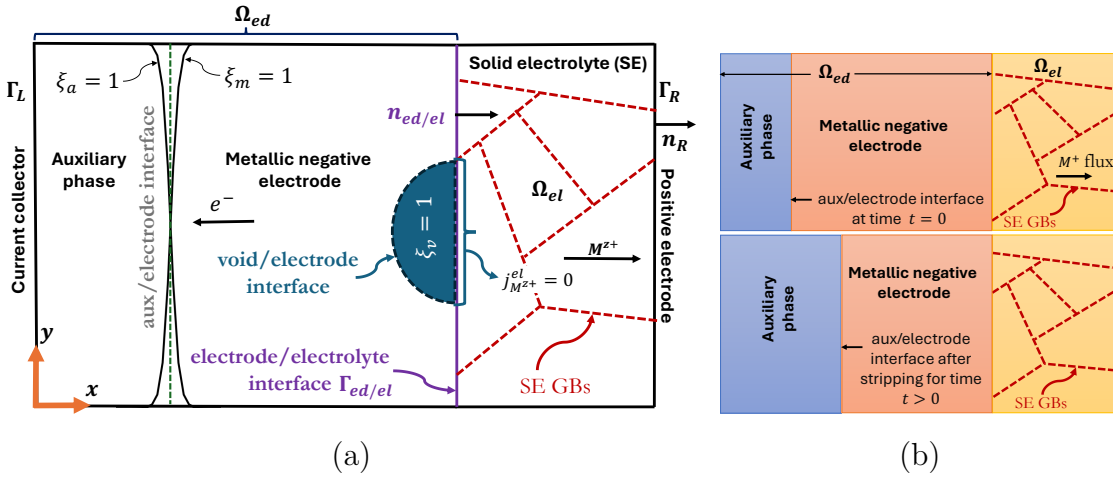
We aim to model two processes occurring in a solid-state cell with a metallic negative electrode. First, we want to simulate the shrinkage and growth of the metallic negative electrode during stripping and plating, assuming a perfect contact between the electrode and the solid electrolyte separator. Second, we want to introduce initial voids at the electrode/electrolyte interface and simulate their evolution during stripping and plating while concurrently simulating the evolution of the metallic negative electrode. We assume that void nucleation has already occurred and focus only on void growth and shrinkage. We then wish to use this model to quantify the impact of applied current density and solid-electrolyte grain boundary diffusivity/ionic conductivity on (i) deposition and depletion rates and (ii) void migration and coalescence rates during electroplating and stripping.

In this work, we use the phase-field approach to simulate the shrinkage and growth of the metallic negative electrode during stripping or plating since it does not require explicitly tracking the moving interface. Specifically, we introduce an “auxiliary” phase into our model representing the empty space that is sandwiched between the metallic negative electrode and the current collector using a spatially-varying phase-field variable field,  $\xi_a$  (Fig. 1a). Note that we do not explicitly represent the current collector for simplicity. Likewise, the negative electrode is modeled using a variable field,  $\xi_m$ . These variables equal 1 in their corresponding phases and 0 elsewhere. They smoothly vary across a submicron-thick diffuse aux/electrode interface region, loosely indicated by a grey dotted line in Fig. 1a. On the other hand, the solid electrolyte does not change and the electrode/electrolyte interface is modeled as stationary and sharp, as indicated by a solid purple line in Fig. 1a. Consequently, the negative electrode grows or shrinks at the cost of the auxiliary phase due to the movement of this diffuse aux/electrode interface instead of the electrode/electrolyte interface, as is done in electrochemical models with liquid electrolytes [44, 46, 47]. This is shown schematically in Fig. 1b.

Moreover, the interfacial voids are modelled using a variable field,  $\xi_v$ , that equals 1 in a void and 0 elsewhere. A dotted blue line indicates the diffuse void/electrode interface in Fig. 1a. Note the voids are purposefully placed at the electrode/electrolyte interface, as shown by experiments [19], [28]. Thus, these voids act as barriers to the migration of metal ions across the electrode/electrolyte interface during stripping or plating. Our approach to model voids resembles that of Zhao *et al.* [36]. Nevertheless, unlike their approach, our model can capture both void migration and the evolution of negative electrodes simultaneously during stripping or plating without explicitly tracking the electrode/electrolyte interface. Further, unlike [36], we also consider the impact of solid electrolyte grain boundaries on

void evolution. We employ the phase-field approach to model these grain boundaries, as indicated by dotted red lines in Fig. 1a. We assume these boundaries to be static since we simulate stripping and plating near room temperature (300 K).

We divide our simulation domain into two subregions, as shown in Fig. 1. One region, referred to as  $\Omega_{ed}$ , contains the negative electrode and auxiliary phases, which we simulate with or without void(s). The other region corresponds to the solid electrolyte separator, referred to as  $\Omega_{el}$ . The static electrode/electrolyte interface lies between these two subregions and is indicated as  $\Gamma_{ed/el}$  in Fig. 1a. The following subsections provide the electrode/electrolyte interfacial conditions and the governing equations in the two subregions. The governing equations are derived for a generic pure alkali metallic negative electrode. We hereafter refer to the diffusing metal atoms by the letter  $M$ . During stripping, the metal atom oxidises at the electrode/electrolyte interface as  $M(ed) \rightarrow M^{z+}(el) + ze^-(ed)$ . Subsequently, the metal cation  $M^{z+}$  diffuses through the solid electrolyte separator domain into the positive electrode. These cations migrate in the opposite direction during plating and reduce at the electrode/electrolyte interface. For simplicity, we use a half-cell model and do not mesh the positive electrode.



**Fig. 1.** Schematics demonstrating the functioning of our model, where (a) shows how the domain is subdivided into two subregions:  $\Omega_{ed}$  containing the negative electrode and  $\Omega_{el}$  representing the solid electrolyte separator. The grey and blue dotted lines mark the diffuse aux/electrode and void/electrode interfaces, respectively. The sharp electrode/electrolyte interface is marked with a solid purple line. **Note that the flux of metal cation ( $j_{M^{z+}}^{el}$ ) is zero along the void/electrolyte interface.** (b) The shrinkage of the negative electrode during stripping due to the movement of the aux/electrode interface under an **applied current density**.

### 2.1. Negative electrode and auxiliary region with a void

We must first define an energy functional to derive the evolution equations for the phase-field variables representing the metallic negative electrode, auxiliary phase and void. This work follows the grand-potential-based phase-field formulations [48, 49] and can be regarded as a special case of the general phase-field model proposed by Aagesen *et al.* [50], incorporating three phases and one diffusing component. Furthermore, our formulation is similar to a recent electrochemical molten salt corrosion model [51]. These formulations assume that the phases have equal diffusion potential in the diffuse interfacial regions but have different phase compositions, similar to the Kim-Kim-Suzuki model [52]. This assumption is important because it separates the interfacial and bulk driving forces required to model microstructures at the micrometer length scales [48]. Specifically, the grand-potential functional,  $\Psi^{ed}$ , is defined as

$$\Psi^{ed} = \int_{\Omega_{ed}} \left[ \sum_{\substack{p= \\ a,m,v}} \frac{\alpha}{2} (\nabla \xi_p)^2 + m \left\{ \sum_{\substack{p= \\ a,m,v}} \left( \frac{\xi_p^4}{4} - \frac{\xi_p^2}{2} \right) + 1.5 (\xi_a^2 \xi_m^2 + \xi_a^2 \xi_v^2 + \xi_m^2 \xi_v^2) + \frac{1}{4} \right\} + \omega_{bulk}^{ed} \right] dV \quad \text{in } \Omega_{ed}, \quad (1)$$

where  $\alpha$  is the gradient-energy coefficient,  $m$  is the barrier height, and  $\omega_{bulk}^{ed}$  is the bulk grand potential density.  $\alpha$  and  $m$  are calculated using the interfacial energy  $\gamma$  and interface width  $l_w$  according to the relations [53]:  $\alpha = (3/4)\gamma l_w$  and  $m = 6.0(\gamma/l_w)$ . The bulk grand potential density is defined as:

$$\omega_{bulk}^{ed} = \sum_{\substack{p= \\ a,m,v}} h_p^{ed} \omega_p = h_a^{ed} \omega_a + h_m^{ed} \omega_m + h_v^{ed} \omega_v \quad \text{in } \Omega_{ed}, \quad (2)$$

where  $\omega_a$ ,  $\omega_m$  and  $\omega_v$  are the bulk grand potential densities of the auxiliary, negative electrode and void phases, respectively. The bulk grand potential density of a given phase is defined as [48]:

$$\omega_p(\mu_M^{ed}) = f_p(\mu_M^{ed}) - \mu_M^{ed} \frac{c_M^p(\mu_M^{ed})}{v_m}, \quad p = a, m, v \quad \text{in } \Omega_{ed}, \quad (3)$$

where  $v_m$  is the molar volume of the metal,  $\mu_M^{ed}(\mathbf{x}, t)$  is the diffusion potential of the metal  $M$  in the region  $\Omega_{ed}$ ,  $f_{p=a,m,v}(\mu_M^{ed})$  and  $c_M^{p=a,m,v}(\mu_M^{ed})$  are the free energy densities and phase mole fractions of the auxiliary phase, metallic negative electrode, and the void, respectively. Note that these properties are functions of the metal diffusion potential because it is the independent variable in a grand-potential-

based model [48].  $h_p^{ed}$  is the interpolation function, which is defined as follows [53]:

$$h_p^{ed} = \frac{\xi_p^2}{[\xi_a^2 + \xi_m^2 + \xi_v^2]}, \quad p = a, m, v \quad \text{in} \quad \Omega_{ed} \quad (4)$$

By taking the variational derivative of Eq. (1) and using the Allen-Cahn equation [54], it follows that the phase-field variables  $\xi_{p=a,m,v}$  evolve according to:

$$\frac{\partial \xi_p}{\partial t} + L_\phi \left[ m \left\{ \xi_p^3 - \xi_p + 3\xi_p \sum_{\substack{q=a,m,v \\ q \neq p}} \xi_q^2 \right\} - \alpha \nabla^2 \xi_p + \sum_{q=a,m,v} \frac{\partial h_q^{ed}}{\partial \xi_p} \omega_q \right] = 0 \quad p = a, m, v \quad \text{in} \quad \Omega_{ed}, \quad (5)$$

where  $L_\phi$  denotes the phase-field kinetic coefficient assumed to be a constant and equal for all phases for simplicity.

We assume that the flux of metal atoms in the region  $\Omega_{ed}$ , i.e.,  $\mathbf{j}_M^{ed}$ , is directly proportional to the gradient in the diffusion potential of the metal atoms. This yields:

$$\mathbf{j}_M^{ed} = - \left[ \frac{(h_a^{ed} M_a + h_m^{ed} M_m + h_v^{ed} M_v)}{v_m} \nabla \mu_M^{ed} \right] \quad \text{in} \quad \Omega_{ed}, \quad (6)$$

where  $M_a$ ,  $M_m$  and  $M_v$  denote the mobilities of the metal in the auxiliary phase, negative electrode and void, respectively. Further, these mobilities are related to the diffusivities using the relation  $M_p = D_M^p dc_M^p / d\mu_M^{ed}$ , where  $dc_M^p / d\mu_M^{ed}$  is the inverse of the thermodynamic factor or susceptibility [48] of phase  $p$ . The thermodynamic factor of a phase  $p$  is defined as the second derivative of the free energy density of a phase with respect to the phase mole fractions [55] and is denoted as  $d\mu_M^{ed} / dc_M^p = v_m d^2 f^p / (dc_M^p)^2$ . Moreover, it should be noted that Eq. (6) in the bulk of the negative electrode, i.e.,  $\xi_m = 1$ , reduces to  $\mathbf{j}_M^{ed} \big|_{\xi_m=1} = -(D_M^p / v_m) \nabla c_M^{ed} \big|_{\xi_m=1}$  (see Appendix A.1), that is the flux of metal species is directly proportional to its concentration gradient. This shows that our flux relation is identical to other approaches if metal diffusion inside the electrode is considered (see, for instance, [56–58]). Moreover, the flux in Eq. (6) must obey the mass conservation equation, which reads:

$$\frac{1}{v_m} \frac{\partial c_M^{ed}}{\partial t} + \nabla \cdot \mathbf{j}_M^{ed} = 0 \quad \text{in} \quad \Omega_{ed}. \quad (7)$$

We, however, do not directly solve for Eq. (7). Several grand-potential-based phase-field formalisms

[48, 59–61] have formulated an evolution equation for diffusion potential from Eq. (7). In this work, we take a similar approach. Thus, Eq. (7) may be equivalently written as follows (see Appendix A.2 for the derivation):

$$\left[ \sum_{\substack{p= \\ a,m,v}} \frac{dc_M^p}{d\mu_M^{ed}} \frac{h_p^{ed}}{v_m} \right] \frac{\partial \mu_M^{ed}}{\partial t} + \nabla \cdot \mathbf{j}_M^{ed} + \sum_{\substack{p= \\ a,m,v}} \left( \sum_{q=a,m,v} \frac{\partial h_p}{\partial \xi_q} \frac{\partial \xi_q}{\partial t} \right) \frac{c_M^p}{v_m} = 0 \quad \text{in } \Omega_{ed}, \quad (8)$$

Thus, we obtain the diffusion potential of metal in the region  $\Omega_{ed}$  by solving Eq. (8) in combination with the flux relation Eq. (6).

Moreover, we assume that electrons are the sole charge-carrying species in the auxiliary phase, negative electrode, and void region. Thus, Ohm's law gives the electric current density in the region  $\Omega_{ed}$ , i.e.,  $\mathbf{i}^{ed}$ :

$$\mathbf{i}^{ed} = -(\sigma_a h_a^{ed} + \sigma_m h_m^{ed} + \sigma_v h_v^{ed}) \nabla \phi^{ed} \quad \text{in } \Omega_{ed}, \quad (9)$$

where  $\sigma_a$ ,  $\sigma_m$  and  $\sigma_v$  are the electronic conductivities of the auxiliary phase, metallic negative electrode, and void phases, respectively, and  $\phi^{ed}$  is the electric potential in the region  $\Omega_{ed}$ . Since charge must be conserved, the electric potential is obtained by solving the charge conservation equation assuming that there are no free charges in the region  $\Omega_{ed}$ , which yields [58]:

$$\nabla \cdot \mathbf{i}^{ed} = 0 \quad \text{in } \Omega_{ed}. \quad (10)$$

It is important to note that, although the governing equations for the diffusion potential and the electric potential are not directly derived from the grand-potential functional,  $\Psi^{ed}[\xi_p, \mu_M^{ed}]$ , this does not render our model non-variational. The functional is dependent only on the phase-field variables  $\xi_{p=a,m,v}$  and the diffusion potential of metal atoms in the electrode  $\mu_M^{ed}$ . The variational derivative with respect to these variables results in Eqs. (5) and (A.2), thereby ensuring that the model is variational. Equation (A.2) is incorporated into the final form of the mass conservation equation, specifically Eq. (8). The mass conservation equation, Eq. (7), and the constitutive equation for mass flux, Eq. (6), are independent equations that are not derived from the minimization of an energy functional. This assertion is equally valid for the charge conservation equation, Eq. (10), and the constitutive equation for current, Eq. (9). Furthermore, unlike Refs. [51, 59, 62], our formulation ignores the electrostatic energy contribution to the energy functional. This is because, within each electrode phase, the charge

density is zero ( $\rho^{ed} = 0$ ) since the metal atoms are the sole diffusing species in the electrode.

## 2.2. Solid electrolyte separator region

We model the solid electrolyte separator as a single-ion conductor and ignore any concentration gradient because Na- $\beta$ -alumina solid electrolytes generally exhibit a transference number close to unity [63, 64]. Consequently, we solve only the charge conservation equation inside the solid electrolyte. Ignoring free charges, the charge conservation equation may be written as [36] [58] [46]:

$$\nabla \cdot \mathbf{i}^{el} = 0 \quad \text{in } \Omega_{el}, \quad (11)$$

where  $\mathbf{i}^{el}$  is the ionic current density in the solid electrolyte. As we ignore concentration gradients in the solid electrolyte, the ionic current density is simply given by Ohm's law [58], [46]:

$$\mathbf{i}^{el} = - \left[ \kappa_g^{el} (h_g^{el} - h_{gb}^{el}) + \kappa_{gb}^{el} h_{gb}^{el} \right] \nabla \phi^{el} \quad \text{in } \Omega_{el}, \quad (12)$$

where  $\phi^{el}$  is the solid electrolyte electric potential,  $\kappa_g^{el}$  and  $\kappa_{gb}^{el}$  are the ionic conductivities of the grain and grain boundary, respectively. The interpolation functions,  $h_g^{el}$  and  $h_{gb}^{el}$ , denote the solid electrolyte grains and the grain boundaries, respectively. Specifically, we assume that these functions take the following form [65]:

$$h_g^{el} = \frac{\sum_{i=1}^{N_g} (\xi_{gi}^{el})^2}{\sum_{i=1}^{N_g} (\xi_{gi}^{el})^2}, \quad h_{gb}^{el} = 16 \sum_{i=1}^{N_g} \sum_{j>i}^{N_g} (\xi_{gi}^{el})^2 (\xi_{gj}^{el})^2 \quad \text{in } \Omega_{el}, \quad (13)$$

where  $\xi_{gi}^{el}$  represents an order parameter, which assumes a value of 1 inside the grain, varies smoothly across the interfaces and is 0 elsewhere in the bulk. The subscript  $i$  indicates a single grain  $g$  of the solid electrolyte and  $N_g$  is the number of solid electrolyte grains. As we aim to study stripping and plating near room temperature, we assume that the grain boundaries of the solid electrolyte are stationary, that is,  $\partial \xi_{gi}^{el} / \partial t = 0$  for all  $i$ .

## 2.3. Interfacial and boundary conditions

Similar to Zhao *et al.* [36], we assume the current density and electric potential are continuous at



the electrode/electrolyte interface. This yields the following equations:

$$\mathbf{i}^{ed} \Big|_{\Gamma_{ed/el}} \mathbf{n}_{ed/el} = \mathbf{i}^{el} \Big|_{\Gamma_{ed/el}} \mathbf{n}_{ed/el}, \quad (14)$$

$$\phi^{ed} \Big|_{\Gamma_{ed/el}} = \phi^{el} \Big|_{\Gamma_{ed/el}}, \quad (15)$$

where  $\mathbf{n}_{ed/el}$  is the unit normal at the electrode/electrolyte interface that points from the electrode to the electrolyte (Fig. 1a). Equation (15) implies that our model does not consider charge transfer or activation overpotential at the electrode/electrolyte interface.

Moreover, the flux of metal cations,  $\mathbf{j}_{M^{z+}}^{el}$ , in the solid electrolyte must be related to the ionic current density ( $i^{el}$ ) by Faraday's law, that is,  $\mathbf{j}_{M^{z+}}^{el} = \mathbf{i}^{el}/zF$  [58], where  $F$  is the Faraday constant and  $z$  is the charge number. Thus, mass conservation at the electrode/electrolyte interface gives:

$$\mathbf{j}_M^{ed} \Big|_{\Gamma_{ed/el}} \mathbf{n}_{ed/el} = \mathbf{j}_{M^{z+}}^{el} \Big|_{\Gamma_{ed/el}} \mathbf{n}_{ed/el} = \left( \mathbf{i}^{el}/zF \right) \Big|_{\Gamma_{ed/el}} \mathbf{n}_{ed/el} = \frac{i_x^{el} \Big|_{\Gamma_{ed/el}}}{zF} \mathbf{n}_{ed/el}, \quad (16)$$

where  $i_x^{el} \Big|_{\Gamma_{ed/el}}$  is the  $x$  component of the solid electrolyte current density. Strictly speaking, the current  $i_x^{el}$ , and thus the flux of metal cations  $\mathbf{j}_{M^{z+}}^{el}$ , must be zero at the void/electrolyte interface because no electrochemical reaction, i.e.  $M(ed) \rightarrow M^{z+}(el) + ze^-(ed)$ , occurs at this interface [36]. However, the flux at the void/electrolyte interface may not always be exactly zero because the conductivity of the void phase is not exactly zero in our model (Table 1). In our simulations, we found that this leads to poor numerical convergence and causes the metal concentration  $c_M^{ed}$  in the void to be significantly lower than zero during stripping. Therefore, to avoid this issue, we multiply the current  $i_x^{el}$  by  $(1 - \xi_v \Big|_{\Gamma_{ed/el}})$ , where  $\xi_v \Big|_{\Gamma_{ed/el}}$  is the void phase field variable at the interface  $\Gamma_{ed/el}$ . This ensures that the flux is always zero along the void/electrolyte interface. In addition, the electric potential is set to zero at the leftmost boundary,  $\Gamma_L$ , which indicates the electrode/current collector interface (Fig. 1a):

$$\phi^{ed} \Big|_{\Gamma_L} = 0. \quad (17)$$

To simulate galvanostatic charging/discharging conditions, we apply a current density  $i_{app}$  at the rightmost solid electrolyte separator boundary as follows:

$$\mathbf{i}^{el} \Big|_{\Gamma_R} \mathbf{n}_R = i_{app}, \quad (18)$$

where  $\mathbf{n}_R$  is the unit normal at the rightmost solid electrolyte separator boundary. Except for this non-homogenous natural boundary condition, we assume zero flux boundary conditions at all external surfaces for all variables.

It is worth noting that it is possible to develop a unified grand-potential model for the entire system, specifically  $\Omega_{ed} + \Omega_{el}$ , by assuming the electrode/electrolyte as a diffuse interface and considering the electrolyte as a distinct phase within the system, as demonstrated in Refs. [59], [51], [66]. The obvious advantage of such a formulation is that it obviates the need to explicitly enforce the interfacial boundary conditions at the electrode/electrolyte interface, specifically Eqs. (14) – (16). However, a potential drawback would be that the concentration/diffusion potential evolution equation within the electrolyte domain has to be solved, thus requiring additional input parameters, such as the free energy density for the solid ceramic electrolyte and ion diffusivities. Given the experimental evidence [63, 64] that  $\beta$ -alumina solid electrolytes are single ion conductors with a transference number approaching unity, solving the concentration evolution equation along with the charge conservation equation would render the model unnecessarily complex because no concentration or diffusion potential gradients can emerge within the solid electrolyte. Another potential limitation is the difficulty in explicitly enforcing the electrochemical boundary conditions at the interface, particularly Eq. (16); even though there are phase-field models [67, 68] capable of explicitly enforcing such interfacial boundary conditions.

### 3. Numerical method and model parameters

Equations (5), (8), (10), and (11) are the governing equations of the model in the two subregions  $\Omega^{ed}$  and  $\Omega^{el}$ . The variables in the two subregions are connected through the interfacial conditions at the electrode/electrolyte interface, i.e., Eqs. (14), (15) & (16). We have implemented these equations in the Multiphysics Object-Oriented Simulation Environment (MOOSE) framework, an open-source finite-element-based software [69]. We use the phase-field module in MOOSE [70, 71] to implement the governing equations. We apply a Newton solver with a LU preconditioner to solve these equations implicitly in MOOSE. An adaptive time-stepping scheme is employed to reduce the computation time. The relative and absolute tolerances for convergence are set at  $10^{-8}$  and  $10^{-9}$ , respectively. For numerical convergence reasons, the equations are non-dimensionalized. The dimensionless forms of these equations are provided in Appendix A.3.

To illustrate the utility of our model and verify its implementation, we parameterize the model for a pure metallic Na negative electrode and a Na- $\beta''$ -alumina (NBA) ceramic solid electrolyte separator.

The properties and parameters we use in the model are shown in Table 1. As Table 1 shows, two parameters related to the interfacial properties of the aux/electrode and void/electrode interfaces are assumed in this study. The first is the interface width, which is an independent parameter chosen to ensure that the computational costs of the simulations remain feasible [48]. The second is the phase-field kinetic coefficient  $L_\phi$ , which is known to influence the rate of void evolution [36]. In this study, this parameter was selected so that the evolution of the electrode or void is diffusion-limited rather than reaction-limited. However, this parameter can be optimized in future studies while comparing model predictions such as cell failure time and void/pore depth against experimental data, as in Ref. [37].

Next, we discuss the chemical grand potential densities defined in Eq. (3). For simplicity, we assume that the chemical free energies of the auxiliary phase, Na negative electrode, and void have parabolic forms, i.e.,  $f_p = A^p/2(c_{Na}^p - c_{Na}^{eq,p})^2$  for  $p = a, m, v$ . Using this expression, the chemical grand-potential densities in Eq. (3) may be expressed as:  $\omega_p = - \left[ (\mu_{Na}^{ed})^2 / (v_m^2 A^p) + (\mu_{Na}^{ed} c_{Na}^{eq,p}) / v_m \right]$  (see Section S.1 of the Supplementary Information). For each phase in  $\Omega^{ed}$ , two parameters are required to calculate these grand potential densities: i) the equilibrium mole fractions of Na,  $c_{Na}^{eq,p}$ , and ii) the parabolic coefficient  $A^p$ . The numerical values of these parameters are provided in Table 1. Note that dilute or ideal solution-free energy expressions could also be used to model these phases. However, employing logarithmic functions for phases with dilute concentrations leads to numerical convergence issues [72], and therefore we use parabolic expressions.

We assume that the Na concentrations in the auxiliary phase and void are negligible compared to the electrode. Specifically, the equilibrium mole fractions of Na in the auxiliary phase and void  $c_{Na}^{eq,a/v}$  are both chosen to be  $10^{-8}$ . The equilibrium mole fraction of Na in the metal phase  $c_{Na}^{eq,m}$  is obtained from the equilibrium vacancy concentration  $c_v^{eq}$  using  $c_{Na}^{eq,m} = 1 - c_v^{eq}$ . Moreover, since there is no experimental data to fit the parabolic free energies, the parabolic coefficients  $A^p$  of the auxiliary phase, negative electrode, and void are chosen to be high enough to ensure Na concentrations inside these phases do not deviate significantly from their equilibrium values during stripping or plating. This assumption is similar to modelling stoichiometric compound phases in phase-field models [72, 73]. Nevertheless, we found that the assumed value of  $A^p$  cannot be arbitrarily high (say  $10^3$  times higher than the values reported in Table 1), because it causes instability in the phase-field variable representing the void phase, which is demonstrated in Section S.13 of the Supporting Information.

The 0 V boundary conditions should be applied at the auxiliary/electrode interface. However, applying a boundary condition at the moving diffuse interface requires changes to the model formulation

[67]. To simplify the model, we apply the 0 V boundary condition at the left boundary and assume that the electronic conductivity in the auxiliary phase equals the Na negative electrode, i.e.,  $\sigma_a = \sigma_m$ . The electronic conductivity of the void phase is taken to be nearly  $10^{-14}$  times smaller than that of the Na negative electrode. The ionic conductivities of the NBA solid electrolyte grains and grain boundaries are calculated from an Arrhenius-type equation [74], i.e.,  $\kappa_p^{el} = (\mathcal{K}_p/T)e^{-E_p/k_B T}$ , where  $p = \{g, gb\}$ . It has been found that the ionic conductivity of NBA grain boundaries is usually lower than that in the grain interior [74]. Nevertheless, it has been reported that the grain boundary conductivity of ceramic solid electrolytes may be enhanced by surface modification [41, 75]. Thus, we also consider a scenario where the grain boundary conductivity is 10 times higher than in the grain interior. Moreover, for simplicity, the Na diffusivity in the auxiliary phase is assumed to be equal to that in the negative electrode, i.e.,  $D_{Na}^a = D_{Na}^m$ . In the void regions, the Na diffusivity is set to 0 (Table 1). **It is worth noting that this study assumes a single-crystal Na electrode. However, polycrystalline metallic electrodes having high-grain boundary diffusivity may enhance the diffusivity of Na within the electrode, as modelled in Ref. [76]. Future studies may extend our model to further investigate this aspect.**

The aux/electrode and void/electrode interfaces have a fixed width  $l_w$  of  $0.5 \mu\text{m}$ . Note that this is also the assumed grain boundary width of the static solid electrolyte grain boundaries. The assumed width is significantly smaller than the mean solid electrolyte grain size, yet almost  $10^3$  times higher than the physical interface width. This results in significantly faster GB transport in the model than would occur in the real system. To compensate for the wide GBs, the GB conductivity can be reduced, as shown in Ref. [65].

We model the behavior in 2D to reduce the computational cost, though the actual void and GB structures are 3D in a real material. The grid spacing  $\Delta x$  is one-third of the interface width to resolve the interface regions accurately. The simulation domain is  $50 \mu\text{m}$  thick, while the solid electrolyte separator is  $18.5 \mu\text{m}$  thick along the x-axis in all the simulations. The domain is  $80 \mu\text{m}$  wide along the y-axis. The simulations are performed on a uniform finite element mesh generated within MOOSE. The 2D mesh is discretized using four-noded quadrilateral elements. The solid electrolyte microstructure is synthetically generated in MOOSE using a Voronoi tessellation and is shown in Fig. S4 of the Supporting Information.

**Table 1**  
Model and numerical parameters used to perform the simulations.

| Parameter                                                          | Value                                                                    | Units                | Refs. |
|--------------------------------------------------------------------|--------------------------------------------------------------------------|----------------------|-------|
| <b>Constants</b>                                                   |                                                                          |                      |       |
| $T$                                                                | 300                                                                      | K                    | —     |
| $R$                                                                | 8.314                                                                    | J/(mol K)            | —     |
| $F$                                                                | 96487                                                                    | C/mol                | —     |
| $z$                                                                | 1                                                                        | —                    | —     |
| $k_B$                                                              | $8.62 \times 10^{-5}$                                                    | eV/K                 | —     |
| $v_m$                                                              | 23.78                                                                    | cm <sup>3</sup> /mol | —     |
| <b>Interfacial properties</b>                                      |                                                                          |                      |       |
| $\gamma$                                                           | 0.22                                                                     | J/m <sup>2</sup>     | [77]  |
| $l_w$                                                              | 0.5                                                                      | $\mu m$              | —     |
| $\alpha$                                                           | $(3/4)\gamma l_w$                                                        | J/m                  | [53]  |
| $m$                                                                | $6.0 (\gamma/l_w)$                                                       | J/m <sup>3</sup>     | [53]  |
| $L_\phi$                                                           | $10^{-4}$                                                                | m <sup>3</sup> /Js   | —     |
| <b>Auxiliary-Na-electrode-void</b>                                 |                                                                          |                      |       |
| $c_v^{eq}$                                                         | $e^{-2.0} e^{-0.157/k_B T}$                                              |                      | [78]  |
| $c_{Na}^{eq,a}, c_{Na}^{eq,m}, c_{Na}^{eq,v}$                      | $10^{-8}, 1 - c_v^{eq}, 10^{-8}$                                         | —                    | —     |
| $A^a/f_c, A^m/f_c, A^v/f_c$                                        | 310, 11, 310                                                             | —                    | —     |
| $D_{Na}^m$                                                         | $6.33 \times 10^{-13}$                                                   | m <sup>2</sup> /s    | [79]  |
| $D_{Na}^v$                                                         | 0                                                                        | m <sup>2</sup> /s    | —     |
| $D_{Na}^a$                                                         | $6.33 \times 10^{-13}$                                                   | m <sup>2</sup> /s    | —     |
| $\sigma_m$                                                         | $2.1 \times 10^5$                                                        | S/cm                 | [80]  |
| $\sigma_v$                                                         | $2.1 \times 10^{-9}$                                                     | S/cm                 | —     |
| $\sigma_a$                                                         | $2.1 \times 10^5$                                                        | S/cm                 | —     |
| <b>Na-<math>\beta''</math>-alumina solid electrolyte separator</b> |                                                                          |                      |       |
| $E_g$                                                              | 0.20                                                                     | eV                   | [74]  |
| $E_{gb}$                                                           | 0.35                                                                     | eV                   | [74]  |
| $\mathcal{K}_g$                                                    | $8.537 \times 10^3$                                                      | (S K)/cm             | [74]  |
| $\mathcal{K}_{gb}$                                                 | $4.786 \times 10^3$                                                      | (S K)/cm             | [74]  |
| $\kappa_{(g \text{ or } gb)}^{el}$                                 | $[\mathcal{K}_{(g \text{ or } gb)}/T] e^{-E_{(g \text{ or } gb)}/k_B T}$ | S/cm                 |       |
| <b>Non-dimensionalization and mesh</b>                             |                                                                          |                      |       |
| $\Delta x$                                                         | $l_w/3.0$                                                                | $\mu m$              | —     |
| $l_c$                                                              | $1 \times 10^{-9}$                                                       | m                    | —     |
| $\tau$                                                             | $l_c^2/D_{Na}^m$                                                         | s                    | —     |
| $f_c$                                                              | $RT/v_m$                                                                 | J/m <sup>3</sup>     | —     |

## 4. Results and discussion

In this section, we show the utility of our model by simulating three cases. First, we show the evolution of the negative electrode during stripping and plating, assuming a perfect electrode/electrolyte interface. Second, we simulate stripping and plating, assuming a single interfacial void exists at the electrode/electrolyte interface. Finally, we consider the case in which multiple interfacial voids form at the electrode/electrolyte interface. To assess the impact of GBs, each of these cases is subdivided into two subcases: one with a homogenous solid electrolyte (SE) and another with polycrystalline SEs with low-conductivity and high-conductivity grain boundaries (GBs).

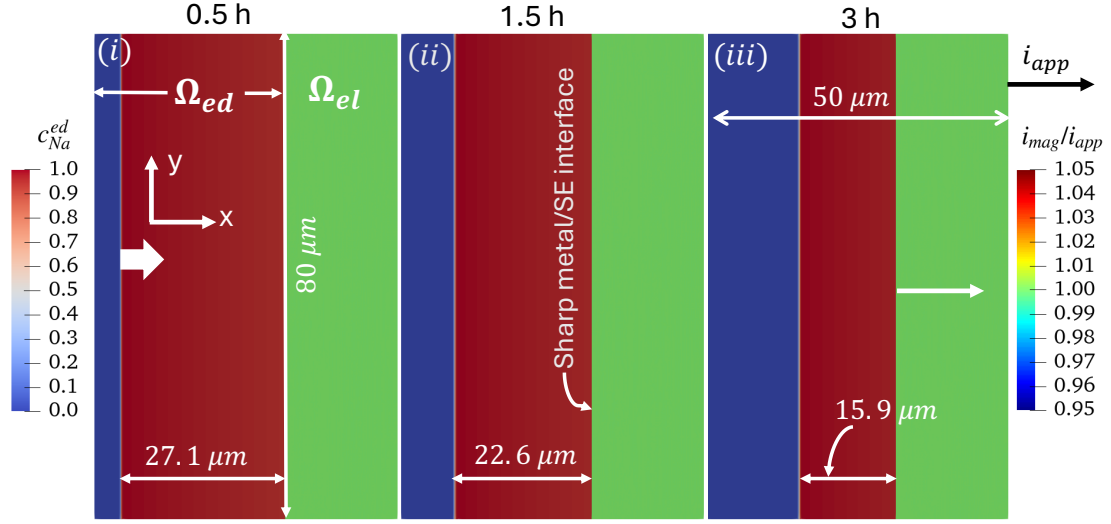
### 4.1. Perfect electrode/electrolyte interface

#### 4.1.1. Stripping and plating simulations with a homogeneous SE

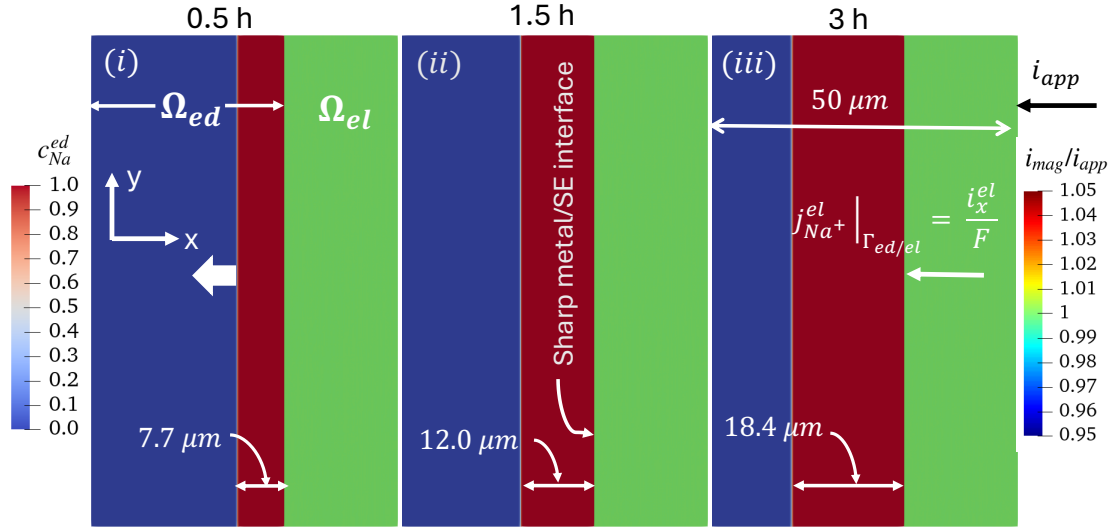
We first simulate the shrinkage and growth of a metallic sodium (Na) negative electrode in perfect contact with a homogeneous SE during stripping and plating for different applied current densities. For validation, we compare our depletion/deposition rates with a sharp interface model [44]. We define the applied current density during stripping or discharge as positive. The applied current density has the same magnitude during plating, but it has the opposite sign. The starting thickness of the negative electrode is  $28.6\text{ }\mu\text{m}$  and  $5.6\text{ }\mu\text{m}$  during stripping and plating, respectively. All stripping and plating simulations are performed for a duration of 3 h.

Figure 2a depicts the shrinkage of the Na negative electrode during stripping for an applied current density of  $0.5\text{ mA/cm}^2$  at 0.5 h, 1.5 h, and 3 h. The diffuse aux/electrode interface moves to the right, causing the negative electrode to shrink during stripping (see also Supplementary Video S1 in the Supporting Information), while the sharp electrode/electrolyte interface remains stationary. Furthermore, we track the position of the moving aux/electrode interface ( $\xi_m = 0.5$ ) in the  $x$  direction over time to quantify the electrode shrinkage rate. Fig. 3a shows that the negative electrode thickness decreases linearly with the stripping time for any applied current density. The slopes or the depletion rates obtained after linear fitting are shown in Fig. 3a and Table 2. These depletion rates are roughly proportional to the applied current density. Thus, the electrode thickness decreases with increasing applied current density after stripping for 3 h, as shown in Fig. 4a.

Figure 2b shows the growth of the Na negative electrode during plating or charging for an applied current density of  $-0.5\text{ mA/cm}^2$  again at 0.5 h, 1.5 h and 3 h. In contrast to stripping, the diffuse aux/electrode interface moves incrementally to the left, causing the growth of the negative electrode

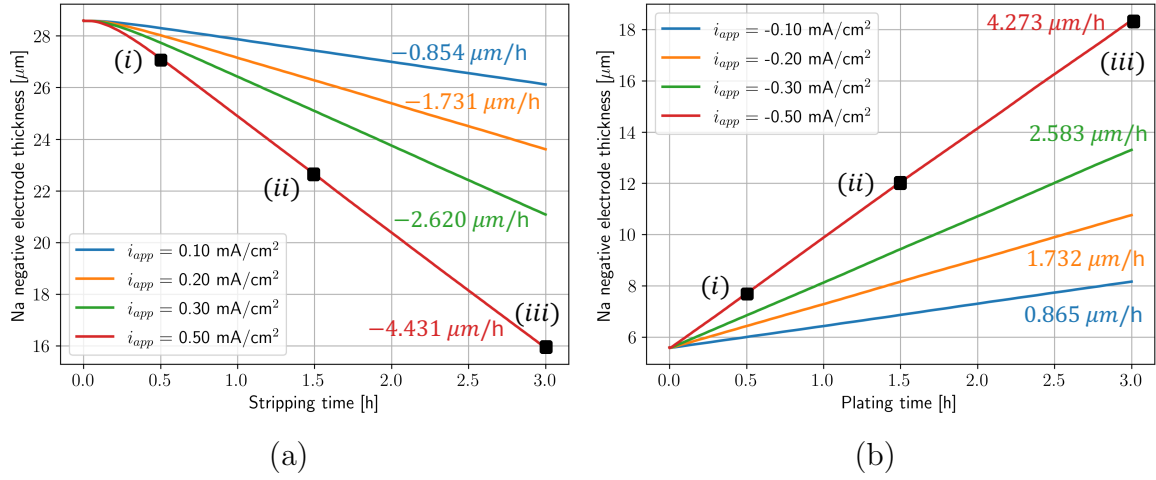


(a)



(b)

**Fig. 2.** (a) Stripping and (b) plating simulations with a perfect electrode/electrolyte interface and a homogeneous SE separator at three different times under an applied current density magnitude of 0.5 mA/cm<sup>2</sup> magnitude.  $\Omega_{ed}$  is shaded by the Na concentration and  $\Omega_{el}$  by the ratio of the local current density to the applied current density.



**Fig. 3.** The variation in the Na electrode thickness with time during (a) stripping and (b) plating. In (a) and (b), the black markers labelled (i)–(iii) correspond to the microstructures shown in Figs. 2a and 2b. Values of the slopes obtained by linear fitting the curves are shown in (a) and (b).

**Table 2**

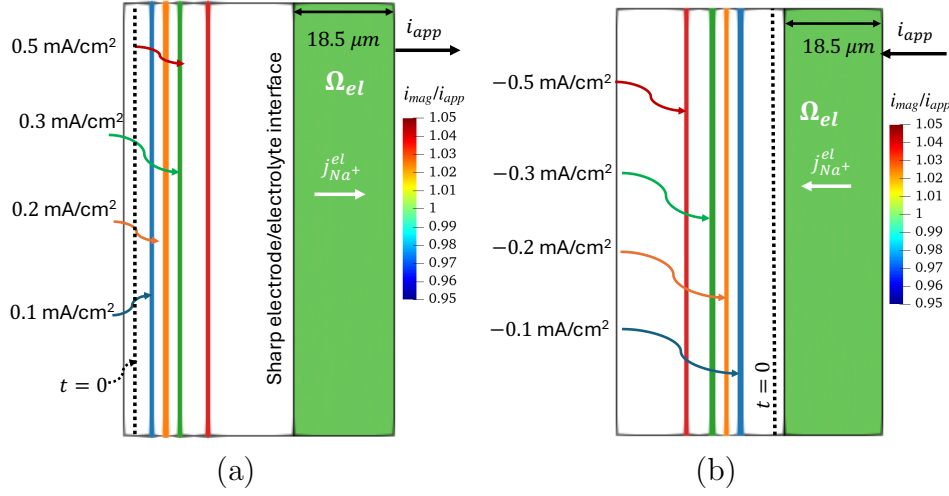
Depletion and deposition rates during stripping and plating calculated using the sharp-interface electrochemical model [44] and our predicted values. The predicted depletion and deposition rates were obtained by linearly fitting the simulated curves shown in Figs. 3a and 3b, respectively.

| $i_{app}$ [mA/cm <sup>2</sup> ]                            | $\pm 0.1$   | $\pm 0.2$   | $\pm 0.3$   | $\pm 0.5$   |
|------------------------------------------------------------|-------------|-------------|-------------|-------------|
| Sharp [ $\mu\text{m}/\text{h}$ ]                           | $\mp 0.885$ | $\mp 1.770$ | $\mp 2.655$ | $\mp 4.425$ |
| Stripping <sup>This paper</sup> [ $\mu\text{m}/\text{h}$ ] | $-0.854$    | $-1.731$    | $-2.620$    | $-4.431$    |
| Plating <sup>This paper</sup> [ $\mu\text{m}/\text{h}$ ]   | $+0.865$    | $+1.732$    | $+2.583$    | $+4.273$    |

during plating (see Supplementary Video S2 in the Supporting Information). As in stripping, we again calculate the Na negative electrode thickness over time by tracking the aux/electrode interface. Fig. 3b shows that the electrode thickness increases linearly with the plating time, and the slopes, i.e. the deposition rates, are shown in Fig. 3b and Table 2. This implies that the final thickness of the electrode increases with increasing magnitude of applied current density (Fig. 4b).

For validation, Table 2 shows the depletion/deposition rates of a sharp interface model [44] (see Section S.2 of the Supplementary Information for details), and they are comparable to those from our model. Table 2 also shows that the difference in the simulated deposition and depletion rates is negligible ( $\leq 2\%$ ) as the applied current densities in the plating and stripping simulations have the same magnitude. In Section S.3 of the Supporting Information, we verify that our model ensures mass and charge conservation by validating it against analytical solutions. Section S.3 also shows that the area-averaged normal flux of Na at the electrode/electrolyte interface remains constant over time and is equal to the ratio of the applied current density to the Faraday constant, i.e.  $i_{app}/F$ , as expected.



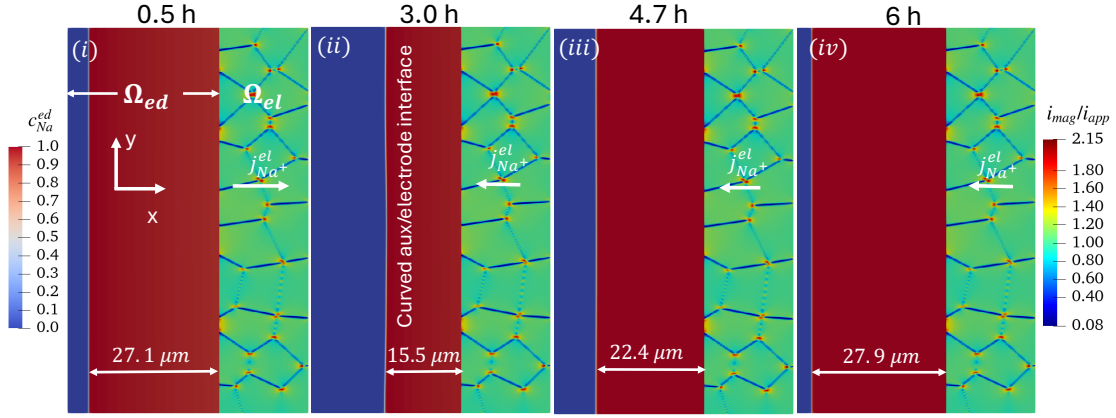


**Fig. 4.** Impact of applied current density on Na electrode thickness during stripping and plating. The aux/electrode interface contour for  $\xi_a = 0.5$  after (a) stripping and (b) plating for 3 h with different applied current densities. The dotted black lines indicate the initial position of the aux/electrode interface. In (a) and (b), the region  $\Omega_{el}$  is shaded by the current density normalized by the applied current density and the arrows indicate the direction of  $\text{Na}^+$  flux,  $j_{\text{Na}^+}^{el}$ .

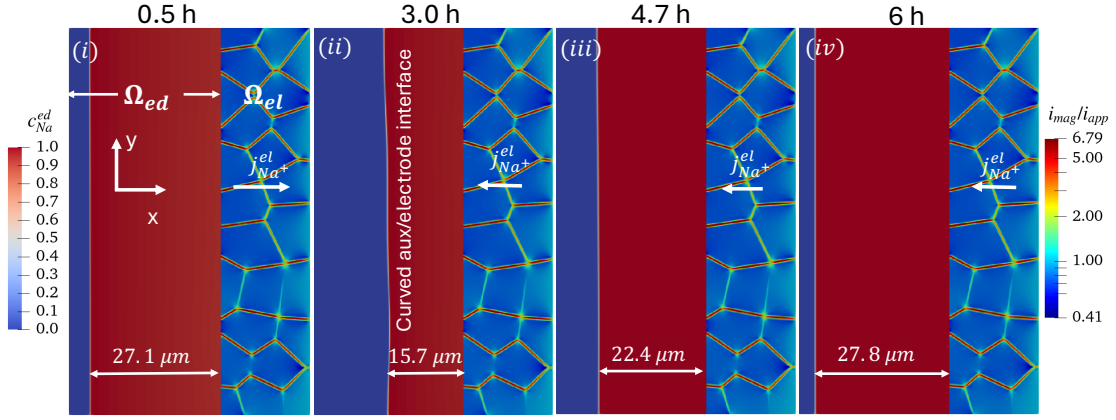
#### 4.1.2. Cyclic simulations with a polycrystalline solid electrolyte (SE)

Next, we investigate the role of the SE GB properties on the deposition and depletion kinetics of the Na-negative electrode during cycling. Specifically, we consider two SEs, one with low-conductivity GBs and the other with high-conductivity GBs. The spatial distributions of ionic conductivities along the GBs and grains for these two SEs are presented in Fig. S4 in Section S.6 of the Supporting Information. We compare the behavior for cases where the conductivity of the GBs is the same as that of the grains ( $\kappa_{gb}^{el}/\kappa_g^{el} = 1$ ), is higher than that of the grains ( $\kappa_{gb}^{el}/\kappa_g^{el} = 10$ ), and is lower compared to the grains ( $\kappa_{gb}^{el}/\kappa_g^{el} = 0.067$ ). It is important to note that the SE grain conductivity ( $\kappa_g^{el}$ ) is the same as that provided in Table 1 in all cases, whereas the SE grain conductivity ( $\kappa_{gb}^{el}$ ) varies.

In our cyclic simulations, we simulate stripping for 3 h and then plating for 3 h under an applied cycling current density of  $0.5 \text{ mA/cm}^2$ . Figures 5a and 5b depict the evolution of the Na negative electrode during cycling in contact with SE having low-conductivity and high-conductivity GBs, respectively (see also Supplementary Videos S3 and S4). The Na negative electrode evolution is similar in both cases, i.e., it shrinks during stripping and grows during plating, as discussed in Section 4.1.1. As before, no concentration gradient of Na occurs in the electrode and the auxiliary phase during cycling. However, the gradient in the diffusion potential of Na ( $\mu_{\text{Na}}^{ed}$ ) within the electrode is non-negligible, as illustrated in Figs. S8a and S8b in Section S.11 of the Supporting Information. Further, this diffusion potential gradient shows nonuniform variation along the electrode/electrolyte interface in both SEs



(a)



(b)

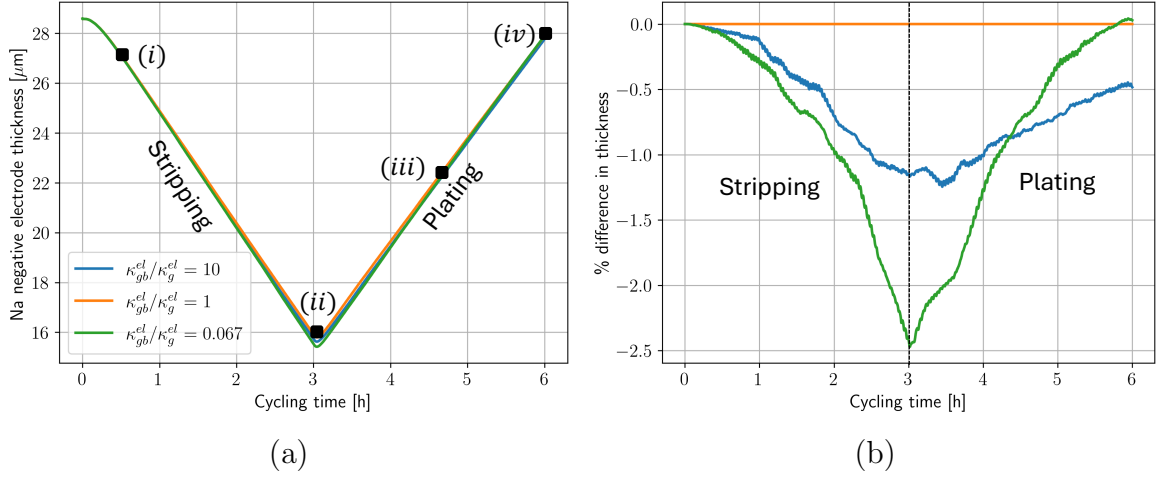
**Fig. 5.** Cycling simulations assuming a perfect electrode/electrolyte interface and polycrystalline SE separator. Evolution of the Na negative electrode during cycling under an applied current density of  $0.5 \text{ mA/cm}^2$  with (a)  $\kappa_{gb}^{el}/\kappa_g^{el} = 0.067$  and (b)  $\kappa_{gb}^{el}/\kappa_g^{el} = 10$ .  $\Omega_{ed}$  is shaded by the Na concentration and  $\Omega_{el}$  by the ratio of the local current density to the applied current density. The arrows indicate the direction of  $\text{Na}^+$  flux,  $j_{Na^+}^{el}$ .

with low-conductivity and high-conductivity GBs, particularly where the SE GB intersects the electrode (Figs. S8a and S8b). This variation is attributed to the nonuniform flux boundary condition at the electrode/electrolyte interface. However, this leads to negligible concentration gradients within the electrode, as these gradients are related to the diffusion potential gradient via  $\nabla c_M^{ed} = \nabla \mu_M^{ed} / (v_m A^m)$ , where  $A^m$  is the parabolic coefficient of the metal phase and  $v_m$  is the molar volume (see Eq. (A.1)). As indicated before, our choice of the parabolic coefficient ensures that the mole fraction of Na within the electrode remains close to the equilibrium value during cycling, irrespective of whether homogeneous or polycrystalline SE separators are employed.

However, in the polycrystalline SE cases, the current density within the SE separator is heterogeneous. Figures 5a and 5b show that the current density is comparatively lower and higher along the GBs than within the grains in the case of low-conductivity and high-conductivity SEs, respectively. It is also evident from Fig. 5a that the SE current density is relatively more concentrated near the triple junctions than within the grains. This is because the charge must be conserved at the triple points [81]. Consequently, the net current entering from any two connected GBs must equal the current leaving through the other connected GB, leading to current concentration near the triple junctions.

Furthermore, the GB width influences the current density within the SE, as the effective ionic conductivity depends on this parameter. The diffuse interface width in our model is selected based on computational considerations and is significantly thicker than the actual width of a GB. Nevertheless, the impact of this choice on effective conductivity can be reduced by employing Eq. (26) from Ref. [65], which demonstrates this method for effective diffusivity.

Moreover, after stripping for 3 h, the aux/electrode interface exhibits a slight curvature in both SEs with low-conductivity (Fig. 5a) and high-conductivity (Fig. 5b) GBs, in contrast to the homogeneous SE case (Fig. 2a). This curvature is attributed to the non-uniform flux distribution along the electrode/electrolyte interface. To confirm this observation, we calculated the thickness of the Na electrode along the  $x$  axis and at the center of the domain. This thickness decreases linearly with time during stripping and then increases linearly during plating (Fig. 6a). The thickness after six hours is close to, but not equal to the original thickness. For the homogeneous SE case, this difference ( $< 1\%$ ) is due to the small nonlinear regions at the start of the simulation and when the system cycles from stripping to plating. The small nonlinear region arises because our simulations start with a sharp aux/electrode interface. This interface gradually becomes diffuse and subsequently begins to migrate in the direction of the applied current density. The change in the thickness with time is marginally



**Fig. 6.** Analysis of the cycling simulations assuming a perfect electrode/electrolyte interface and polycrystalline SE separator. The variation with time of the (a) Na negative electrode thickness, and (b) percentage difference in the electrode thickness relative to the homogeneous SE case. In (a), the black markers labelled (i)–(iv) correspond to the microstructures shown in Fig. 5a.

dependent on the conductivity of the GBs, with the behavior being nearly indistinguishable across all three  $\kappa_{gb}^{el}/\kappa_g^{el}$  ratios. To quantify any potential differences, we calculate the percentage difference in the thickness of the Na electrode relative to the homogeneous SE case (Fig. 6b). The maximum percentage difference is about  $\sim 2.5\%$ , which supports our assertion that the thickness of the Na electrode is marginally impacted by the SE GB conductivity.

Furthermore, Section S.7 of the Supporting Information shows that mass is conserved during cycling with polycrystalline SEs. This section also demonstrates that the variation in the average normal flux at the interface with time is almost equal in the case of SEs with both low-conductivity and high-conductivity GBs when compared to the homogeneous SE case.

#### 4.2. Single void at the electrode/solid electrolyte interface

##### 4.2.1. Stripping and plating simulations with a single-crystal solid electrolyte (SE)

Next, we simulate the evolution of a single void at the electrode/electrolyte interface during stripping for different applied current densities. Similar to Zhao *et al.* [36], we begin all our simulations with a semi-circular void of radius  $4.8 \mu\text{m}$  at the electrode/electrolyte interface. However, unlike Zhao *et al.* [36], the thickness of the negative electrode in our model varies during stripping. The initial Na negative electrode thickness is assumed to be  $28.6 \mu\text{m}$  in all simulations. The simulations are run for a stripping time of 1 h, or until the void completely spans the electrode/electrolyte interface, i.e. complete contact loss occurs. Once complete contact loss occurs, the flux of  $\text{Na}/\text{Na}^+$  at the

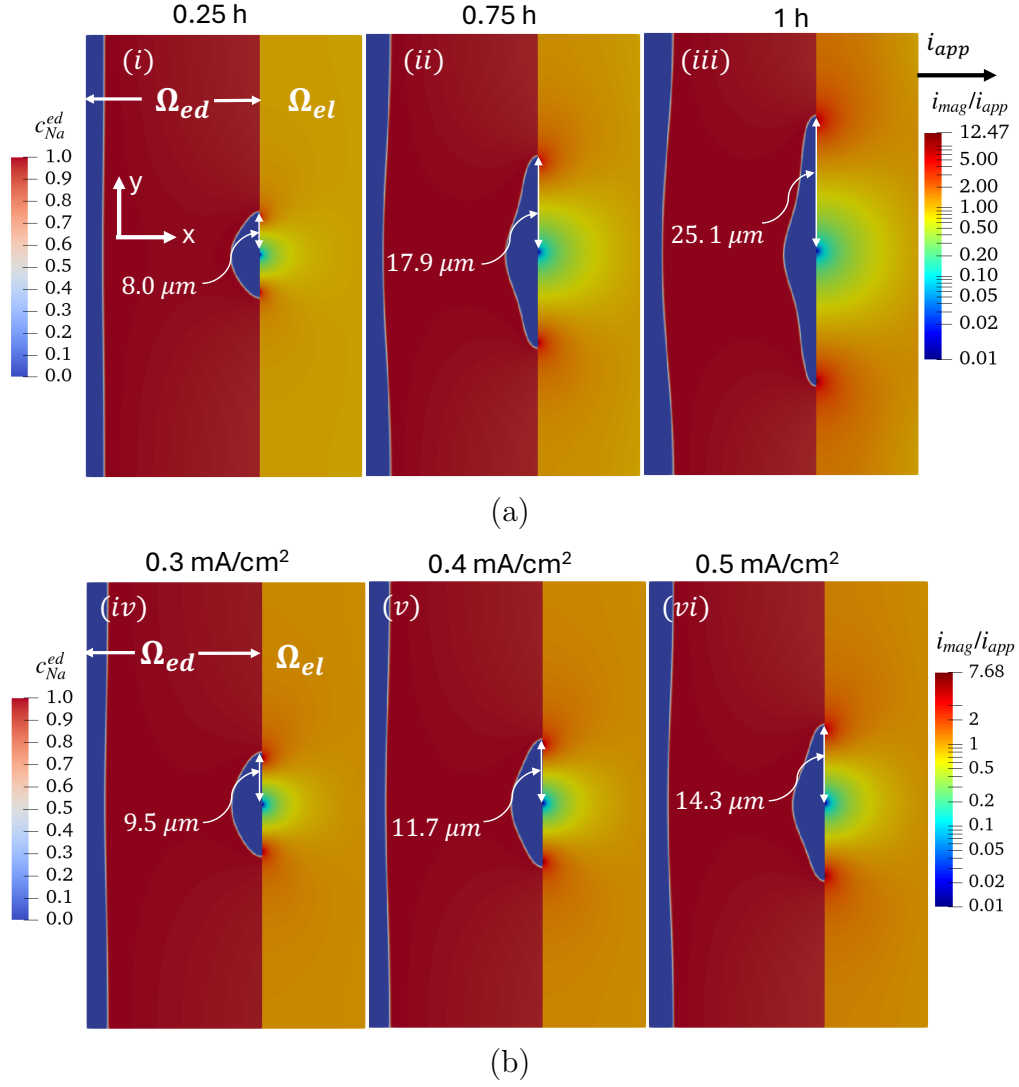
electrode/electrolyte interface ~~becomes~~ effectively **becomes** zero and further stripping cannot occur.

Figure 7a shows the evolution of a single void during stripping under an applied current density of **0.5 mA/cm<sup>2</sup>**. The void grows due to the formation of vacancies at the electrode/electrolyte interface as Na atoms diffuse into the electrolyte during stripping. These vacancies cause the void to change its shape from a semi-circle to a pancake, which qualitatively agrees with the void shapes observed in experiments [19, 28] and void simulations in Li/LLZO system [35, 36]. The void growth normal to the electrode/electrolyte interface is small compared to its growth along the interface. While the negative electrode shrinks during stripping, it shrinks more on the top and the bottom than it does in the center because the void blocks the flux of Na<sup>+</sup> across the electrode/electrolyte interface (**Fig. 7a**). Thus, the aux/electrode interface is no longer flat (see Supplementary Video S5 in the Supporting Information). Also, the current density in the SE separator is higher near the void edges and lower near the void center due to contact loss.

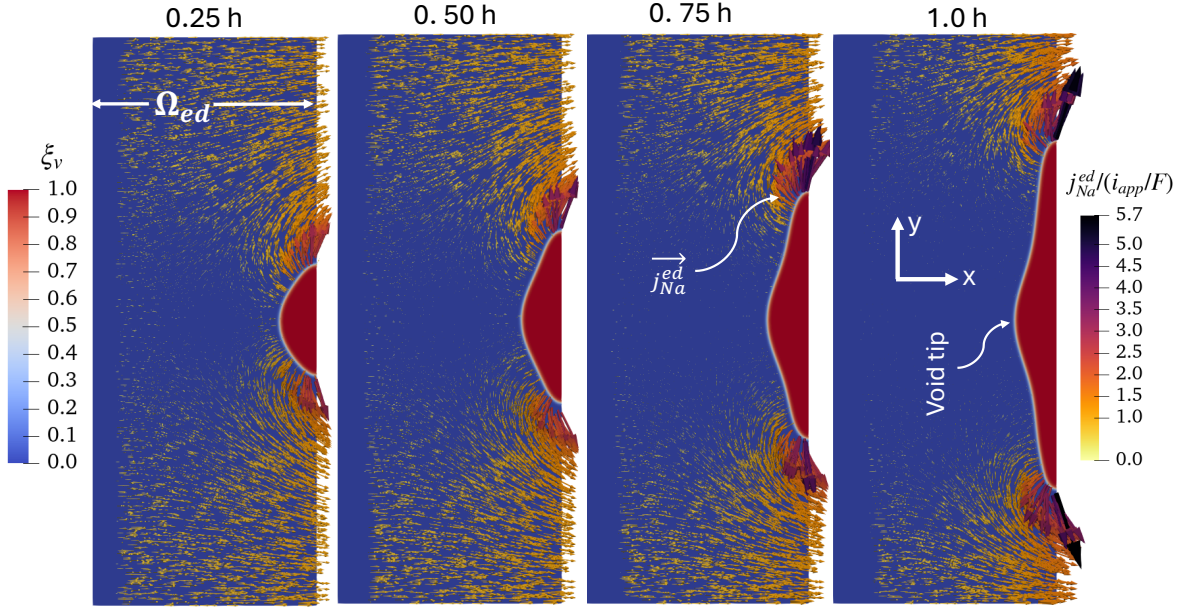
**Figure 8 shows the temporal variation in the distribution and direction of Na flux within the electrode. The Na flux distribution is nonuniform and concentrated near the void edges during stripping. The Na flux is concentrated because the current density within the solid electrolyte is focussed near the void edges, as illustrated in Figure 7a. Consequently, the magnitude of Na flux concentration increases with increasing void size during stripping (Fig. 8). It is also interesting to observe that the Na flux around the void edges is oriented away from the void surface and into the electrolyte (Fig. 8). Since the vacancy flux must be equal in magnitude and opposite to the direction of the Na flux, it implies that the vacancies are flowing into the void edges, causing the void to grow along the electrode/electrolyte interface during stripping. The Na flux around the void tip is almost negligible (Fig. 8), which explains why the void tip shows limited growth normal to the electrode/electrolyte interface. On moving away from the void region and into the electrode, the direction of Na flux becomes increasingly aligned with the  $x$  axis and its magnitude reduces to the flux normalization factor, i.e.,  $i_{app}/F$  (Fig. 8).**

The magnitude of the applied current density has a large impact on the void growth, as shown in Fig. 7b after stripping for 0.6 h. The void shapes and electrode thickness are similar in all cases, but the void size and current constriction increase with increasing applied current density, which is similar to Zhao’s analysis for the Li/LLZO system [36]. **Moreover, the choice of the diffuse interface width influences the final void size and the peak current density within the electrolyte (see Appendix A.4).**

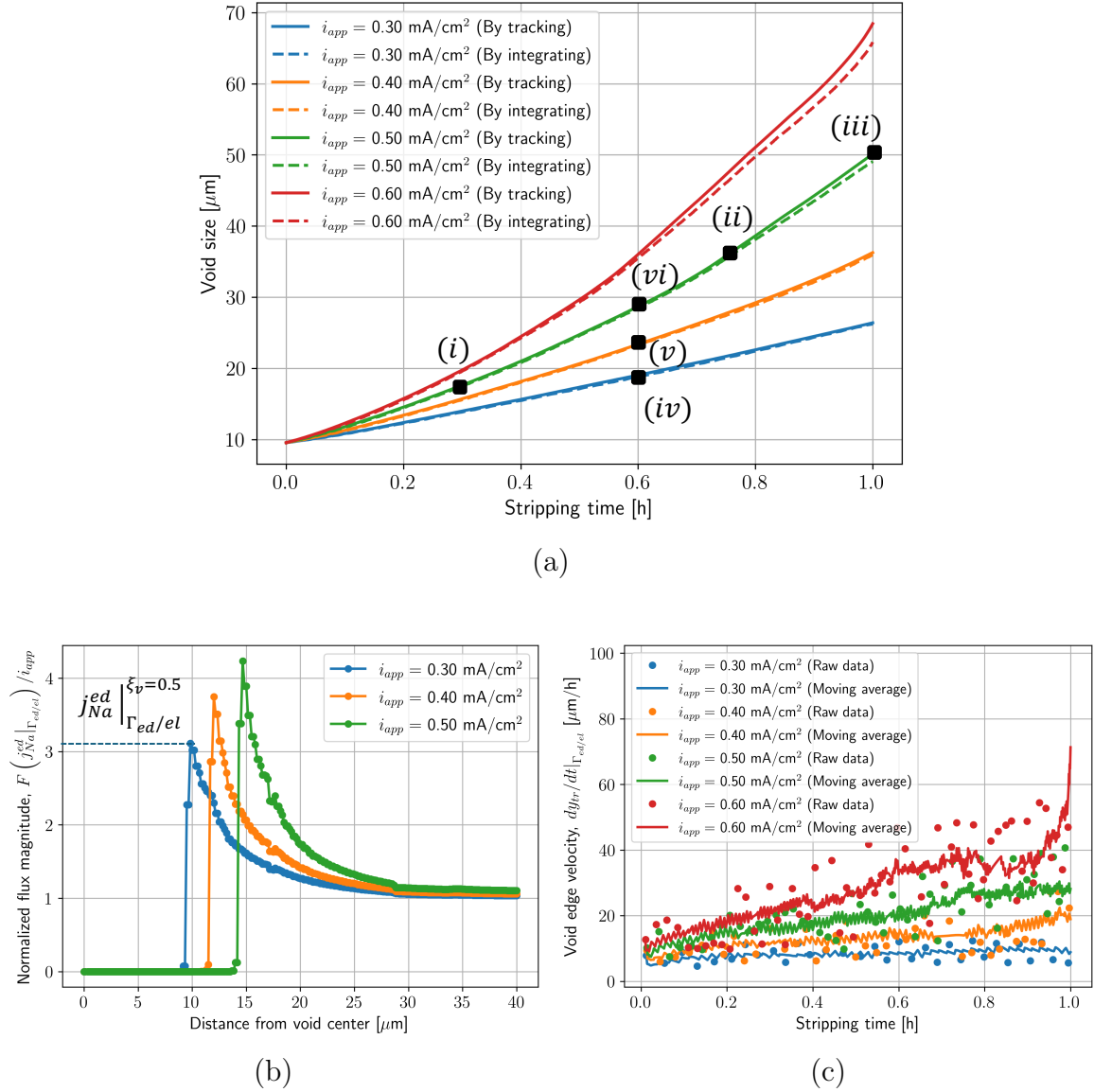
To quantify the void growth rate during stripping, we approximate the void size by doubling the distance from the void edge (the position where  $\xi_v = 0.5$  along the electrode/electrolyte interface) to



**Fig. 7.** Stripping simulations with a single interfacial void at the electrode/electrolyte interface and a homogeneous solid electrolyte separator with different applied current densities. (a) Void evolution with an applied current density of 0.5 mA/cm<sup>2</sup>. (b) Void morphology for different applied current densities after stripping for 0.6 h.  $\Omega_{ed}$  is shaded by the Na concentration and  $\Omega_{el}$  is shaded by the ratio of the local current density to the applied current density.



**Fig. 8.** The temporal variation in the spatial distribution of Na flux within the region  $\Omega_{ed}$  in the presence of a single interfacial void during stripping under an applied current density ( $i_{app}$ ) of 0.5 mA/cm<sup>2</sup>.  $\Omega_{ed}$  is shaded by the phase-field variable,  $\xi_v$ , representing the void phase. The arrow glyphs denote the direction of the Na flux vector ( $\vec{j}_{Na}^{ed}$ ) at a point and are colour-coded according to the magnitude of the flux obtained after normalization. The normalization factor is equal to  $i_{app}/F$ , indicating the flux for a perfect electrode/electrolyte interface. The length of an arrow glyph is proportional to the normalized magnitude of the flux at that point. For clarity, the maximum number of arrow glyphs displayed is fixed at 6500.



**Fig. 9.** Analysis of stripping simulations with a single interfacial void at the electrode/electrolyte interface and a homogeneous solid electrolyte separator with different applied current densities. (a) Void size (twice the distance between the void center and edge along the electrode/electrolyte interface) over time. In (a), the solid lines indicate the actual void size obtained by explicitly tracking the void edge, while the dotted lines are obtained by time integrating the data in (c). The black markers labelled (i)–(vi) correspond to the microstructures shown in Figs. 7a and 7b. (b) The magnitude of the normalized Na flux along the electrode/electrolyte interface after stripping for 0.6 h. The flux magnitude,  $j_{Na}^{ed}$ , is normalized by  $i_{app}/F$ . The dotted horizontal line indicates the void edge flux magnitude for  $i_{app} = 0.3 \text{ mA/cm}^2$ . (c) Void edge velocity calculated using Eq. (19) as a function of stripping time. The solid lines indicate the moving average value over 15 time steps.



the void center. Figure 9a shows the void size with time for different applied current densities. The growth of the void size increases with increasing applied current density, as shown qualitatively in Fig. 7b. The void size grows almost linearly with time at first but then accelerates with time. This acceleration is most clear for the larger applied current densities, i.e., 0.5 and 0.6 mA/cm<sup>2</sup>. The theoretical model of Lu *et al.* [30] assumes a linear void growth rate (see Eq. (7) in Ref. [30]). However, our results indicate that this assumption may not be accurate.

To investigate what controls the void growth rate, we plot the spatial distribution of the magnitude of the Na flux along the electrode/electrolyte interface, i.e.  $j_{Na}^{ed}|_{\Gamma_{ed/el}} = \sqrt{(j_{x,Na}^{ed})^2 + (j_{y,Na}^{ed})^2}$  for three selected applied current densities after stripping for 0.6 h (Fig. 9b). This interfacial flux is normalized by the interfacial flux assuming a perfect interface, that is,  $i_{app}/F$ . The interfacial flux is zero along the void/electrolyte interface, jumps to a maximum at the void edge, and gradually decreases along the electrode/electrolyte interface until it equals the flux in the case of a perfect interface. The void size and the maximum flux value at the edge increase with increasing applied current density. Based on these results, we assume that the maximum interfacial flux at the void edge controls the rate at which the void elongates along the electrode/electrolyte interface, i.e.,  $\Gamma_{ed/el}$ . Specifically,

$$\left. \frac{dy_{tr}}{dt} \right|_{\Gamma_{ed/el}} = \pm 2v_m j_{tr}(t), \quad (19)$$

where  $dy_{tr}/dt|_{\Gamma_{ed/el}}$  is the velocity of the void edge along the electrode/electrolyte interface,  $v_m$  is the molar volume of Na,  $j_{tr}(t) = j_{Na}^{ed}|_{\Gamma_{ed/el}}^{\xi_v=0.5}$  is the magnitude of the flux at the void edge, and  $\pm$  is used to indicate a stripping (+) or plating (−) simulation. The superscript  $\xi_v = 0.5$  indicates the value of the void phase-field variable used to approximate the position of the diffuse void/electrode interface.

Figure 9c depicts the velocity of the void edge obtained using Eq. (19) as a function of time for different applied current densities. The velocities are close to linear for a time and then rapidly accelerate for the larger applied current densities, and we expect similar behavior would be seen with the lower applied current densities if longer times were simulated. We integrate this data with time to estimate the change in the void size and compare it with the actual void size, as shown in Fig. 9a. The approximate void sizes obtained by integrating Eq. (19) compare reasonably well with the actual sizes, though the differences are larger for high applied current densities and stripping durations  $\geq 0.8$  h. One possible explanation for this deviation could be that Eq. (19) does not consider the contact angle between the void, metal electrode and the SE separator. Thus, these results suggest an improved

approach to predicting the void growth than that used by Lu *et al.* [30], but a more quantitative analytical model is still needed to predict the void growth rate, which is beyond the scope of this work.

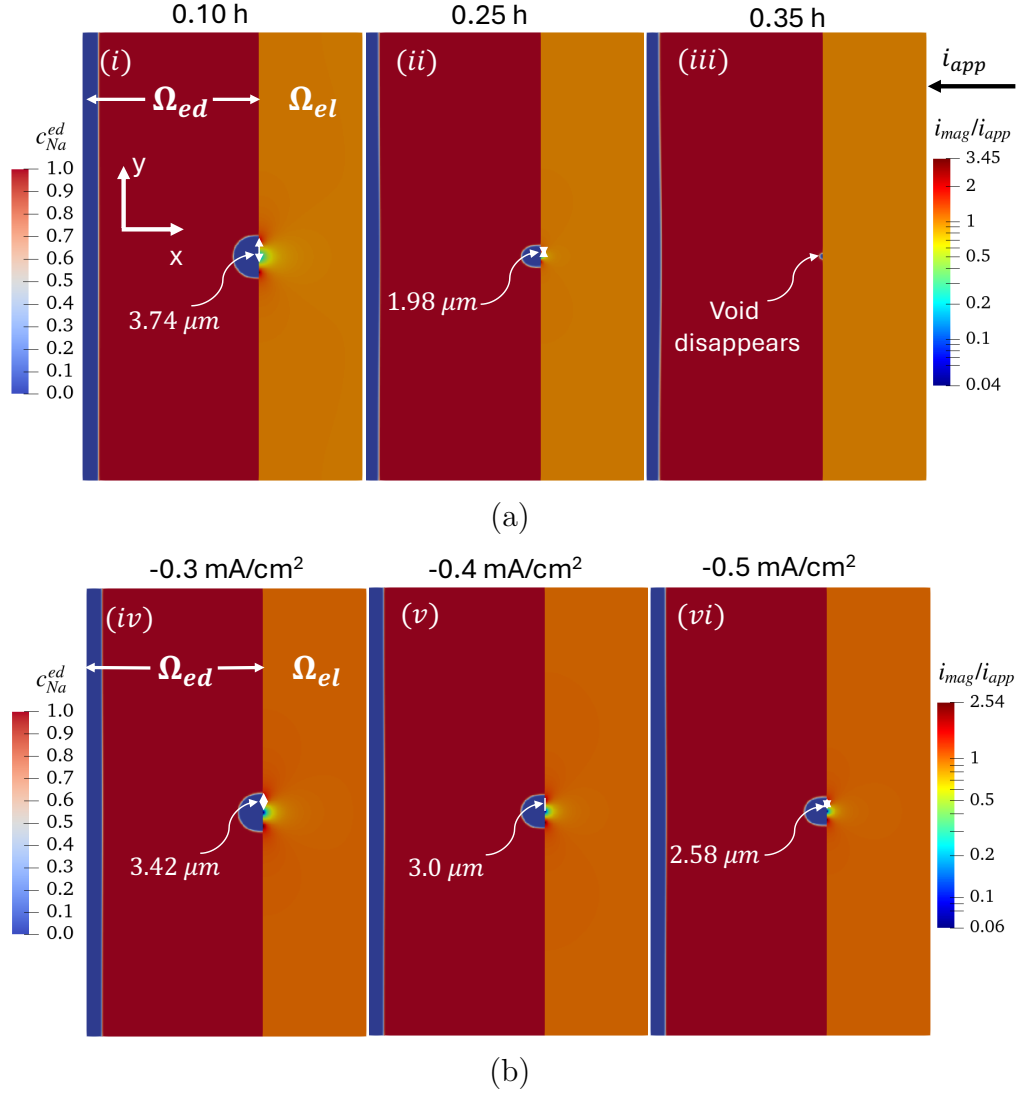
We also simulate the shrinkage of a single void at the electrode/electrolyte interface during plating for 1 h (or once the void completely disappears) for different applied current densities. Like stripping, a semi-circular shaped void of radius  $4.8\text{ }\mu\text{m}$  is placed initially at the electrode/electrolyte interface. The initial width of the Na negative electrode is assumed to be  $28.6\text{ }\mu\text{m}$  in all of our simulations.

Figure 10a shows that the interfacial void preferentially shrinks along the electrode/electrolyte interface during plating for an applied current density of  $-0.5\text{ mA/cm}^2$ , which is consistent with experiments [19], [28] and simulations in Li/LLZO systems [36]. However, unlike Zhao *et al.* [36], our plating simulations indicate that a single void disappears at the end of the plating cycle instead of forming occluded voids, as also observed in the experiments [28]. One possible reason could be that our system and initial void sizes are smaller than those from Zhao’s simulations [36] (system size and initial void radius in [36] is  $80 \times 250\text{ }\mu\text{m}^2$  and  $10\text{ }\mu\text{m}$ , respectively). In addition to void shrinkage, Fig. 10a shows that the negative electrode grows during plating (see also Supplementary Video S6 in the Supporting Information). This growth, however, is limited because the simulation ends after a short time, approximately in  $\leq 0.52\text{ h}$ , i.e., when the void disappears. Once the void disappears, the behavior should be identical to the plating case without a void (Fig. 2b).

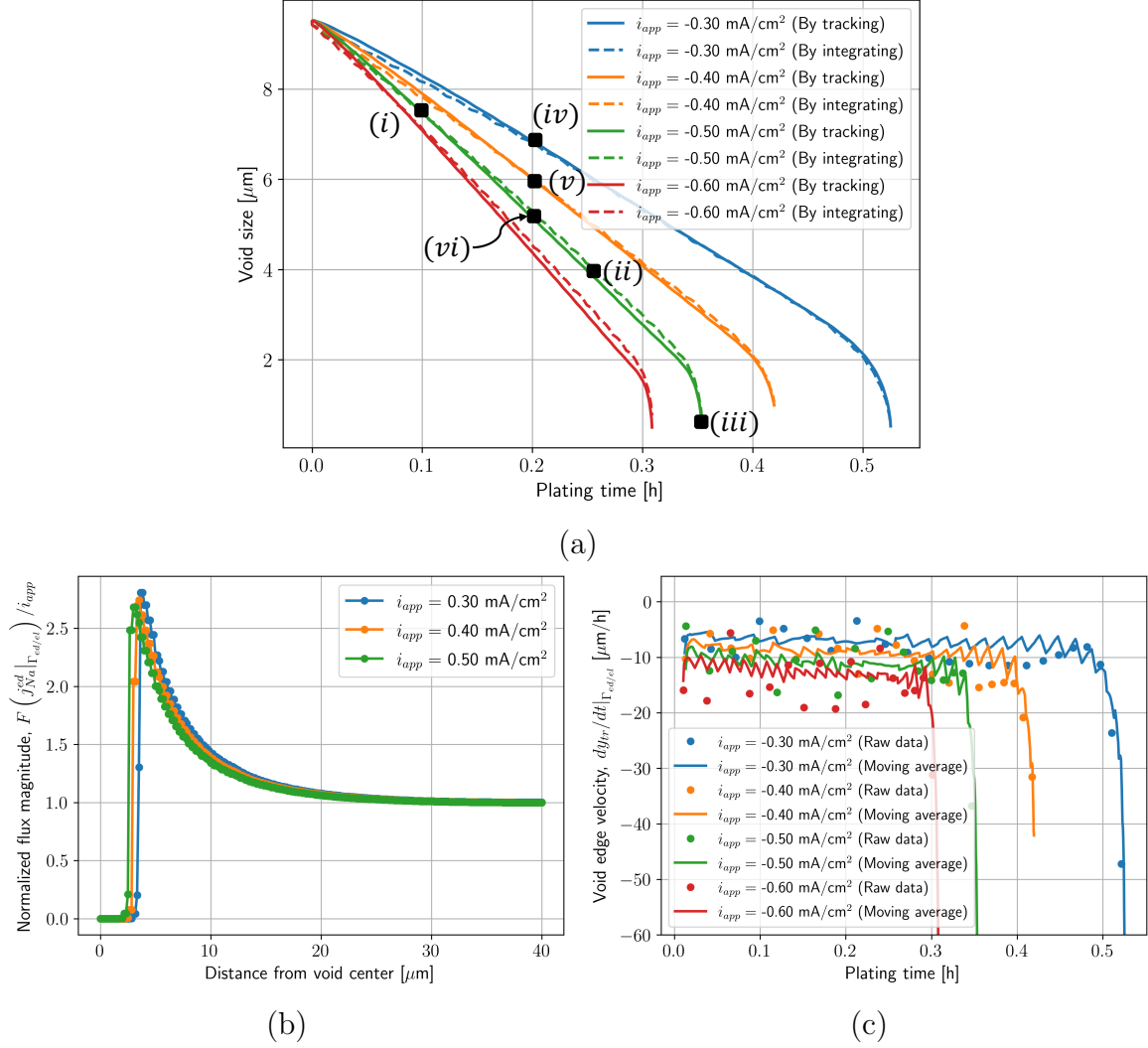
The applied current density has a large impact on the void evolution rate during plating, as shown in Fig. 10b. Although the void evolution is qualitatively similar in all cases, the final void size after plating for 0.2 h decreases with increasing magnitude of the applied current density. This suggests that the void shrinkage rate increases with increasing magnitude of the applied current density.

We further analyse the void shrinkage during plating by plotting the void size with time, similar to our void growth analysis during stripping (see Fig. 11a). The void size decreases linearly with time until the void disappears, and the shrinkage rate increases with the magnitude of the applied current density. As with stripping, we attribute this behaviour to the rate at which the flux of Na at the void edge varies with time. Figure 11b shows the normalized flux of Na along the electrode/electrolyte interface for three applied current densities after plating for 0.2 h. Like with stripping, the Na flux is zero along the void, it then peaks at the edge, and gradually decreases to the flux assuming a perfect interface near the top of the electrode/electrolyte interface.

We again calculate the velocity of the void edge using Eq. (19) by determining the Na flux at the edge,  $j_{tr}(t)$ , as shown in Fig 11c. The velocity is negative because the void size decreases with



**Fig. 10.** Plating simulations with a single interfacial void at the electrode/electrolyte interface and a homogeneous solid electrolyte separator. (a) Void evolution with an applied current density of  $-0.5 \text{ mA/cm}^2$ . (b) Void morphology for different applied current densities after plating for 0.2 h.  $\Omega_{ed}$  is shaded by the Na concentration and  $\Omega_{el}$  is shaded by the ratio of the local current density to the applied current density.



**Fig. 11.** Analysis of plating simulations with a single interfacial void at the electrode/electrolyte interface and a homogeneous solid electrolyte separator. (a) Void size (twice the distance between the void center and edge along the electrode/electrolyte interface) over time. In (a), the solid lines indicate the actual void size obtained by explicitly tracking the void edge, while the dotted lines are obtained by time integrating the data in (c). The black markers labelled (i)–(vi) correspond to the microstructures shown in Fig. 10a and 10b. (b) The magnitude of the normalized Na flux along the electrode/electrolyte interface after plating for 0.2 h. The flux magnitude,  $j_{Na}^{ed}$ , is normalized by  $i_{app}/F$ . (c) Void edge velocity calculated using Eq. (19) as a function of plating time. The solid lines indicate the moving average value over 15 time steps.

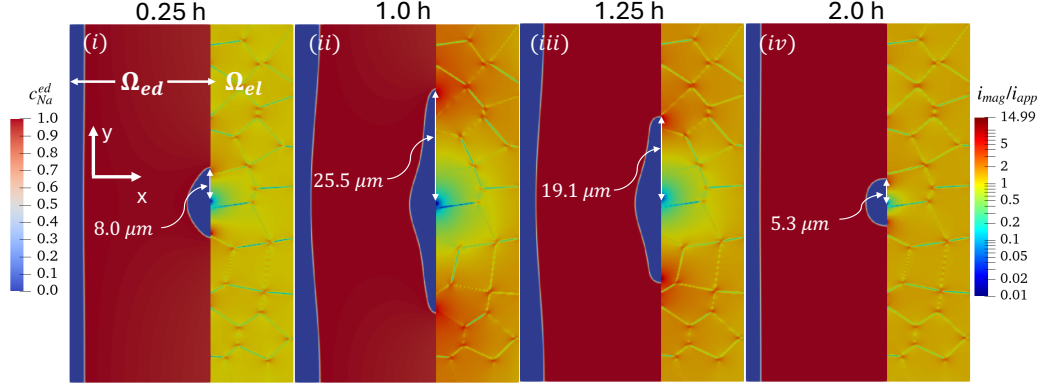
plating time. The magnitude of the edge velocity, and thus, the Na flux at the edge, increases with increasing magnitude of the applied current density. Subsequently, we estimate the void size over time by integrating velocity and the results are shown in Fig. 11a with dotted lines. Our estimated void sizes are in reasonable agreement with the actual void sizes, though the deviation increases with increasing applied current density. This result further supports our argument that the void migration rate is directly proportional to the **magnitude** of the Na flux at the edge.

#### 4.2.2. Cyclic simulations with polycrystalline solid electrolyte (SE) separators

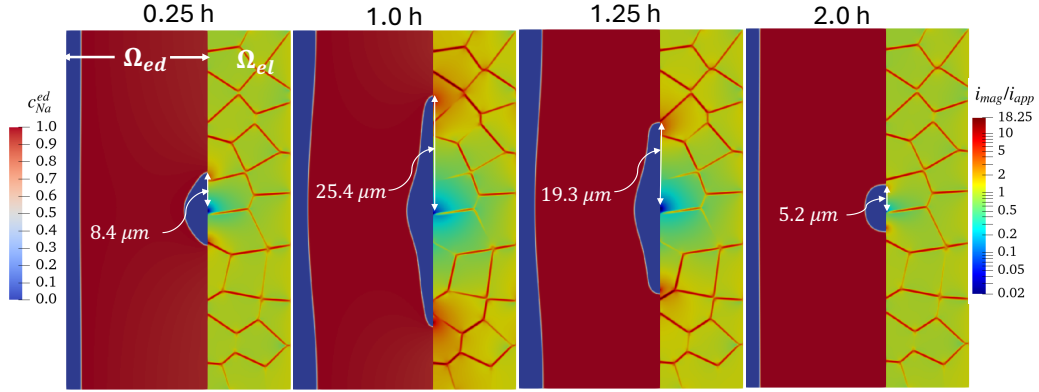
Next, we perform cyclic simulations to investigate the impact of SE GBs on void evolution. The cyclic simulations involve stripping for 1 h and then plating for 1 h at an applied cycling current density of **0.5 mA/cm<sup>2</sup>**. Similar to Section 4.1.2, polycrystalline SEs with low-conductivity and high-conductivity GBs are considered. The initial interfacial void size and thickness of the negative electrode are identical to the cases discussed in Section 4.2.1 for all simulations.

Figures 12a and 12b show the evolution of a single interfacial void during cycling in contact with a SE having low-conductivity and high-conductivity GBs, respectively. The void evolution is almost identical in both cases, i.e., the interfacial void elongates along the electrode/electrolyte interface during stripping for 1 h, which leads to current constriction in the SE separator near the void edges. Subsequently, the void shrinks during plating. Although the Na electrode thickness also varies during cycling, the net change in thickness is small and not apparent in Figs. 12a and 12b. The void size increases during stripping and decreases during plating, and is not significantly changed by the GB conductivity (see Fig. 13a). This is most clear when we plot the percentage change in the void size compared to the case with a homogeneous SE, **as shown in Fig. 13b** for the stripping half (see Fig. S7 in Section S.9 of the Supporting Information for the full cycling plot). The largest deviation is just over **6%**. **Thus, the impact of SE GB conductivity on the overall void evolution is negligible.**

While the impact on the overall void evolution is negligible, there are local effects of the GB conductivity on the void evolution. **Figure 13b shows that, relative to the homogeneous SE case, the void evolution tends to be faster (indicated by peaks in Fig. 13b) as the void upper edge nears a high conductivity GB, whereas it tends to be slower (indicated by troughs in Fig. 13b) as the void upper edge approaches a low-conductivity GB. The slope of the lines in Fig. 13b is a measure of the percentage change in void velocity relative to the homogeneous SE case. An increase or decrease in slope signifies an increase or decrease in void velocity relative to the homogeneous SE case. These deviations in void size result from interactions between the void edge and SE GBs that intersect the**

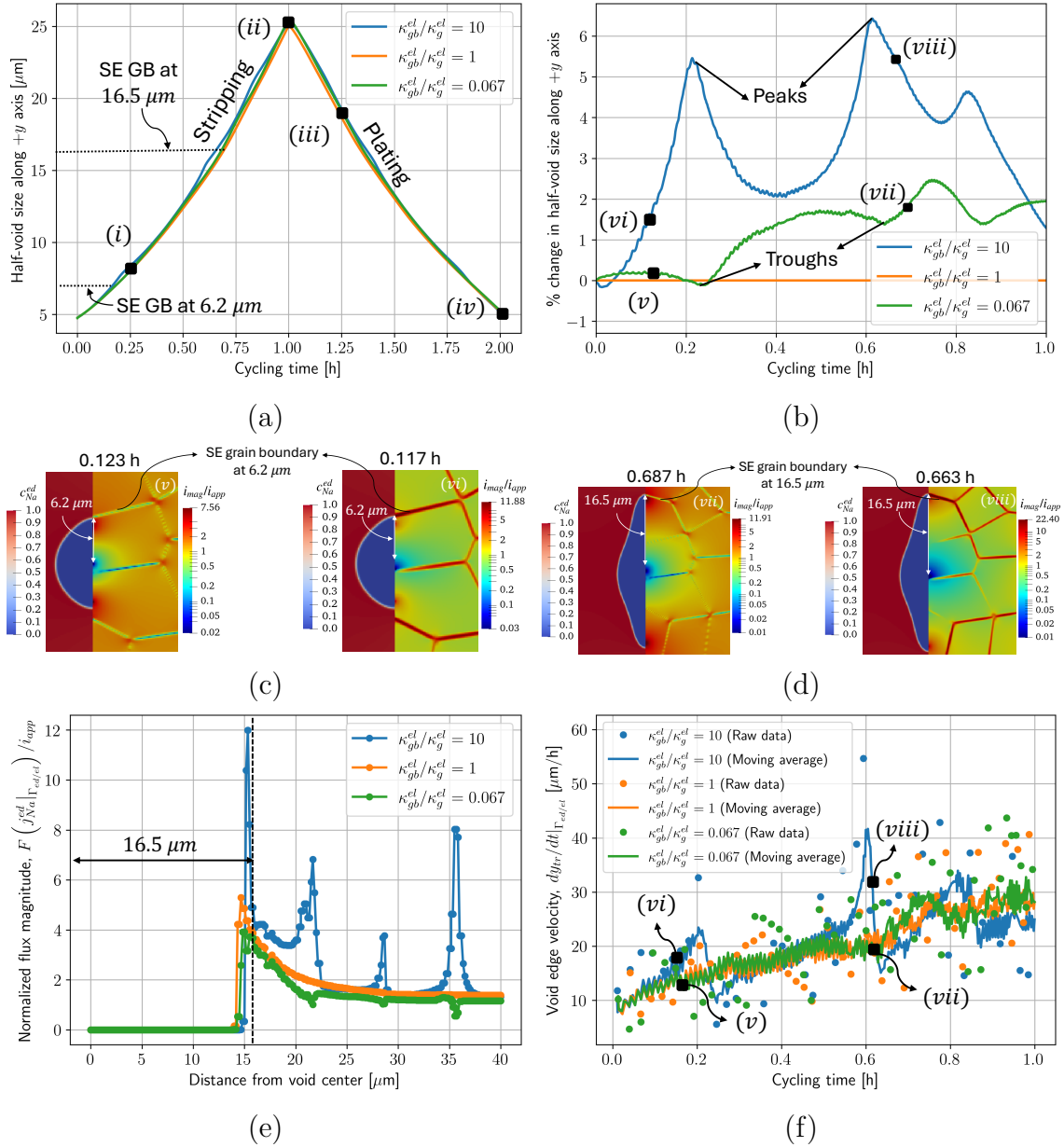


(a)



(b)

**Fig. 12.** Cycling simulations with a single interfacial void at the interface between the negative electrode and a polycrystalline SE separator. Evolution of the void and the negative electrode during cell cycling in solid electrolytes with (a) low-conductivity and (b) high-conductivity GBs under an applied current density of **0.5 mA/cm<sup>2</sup>**.  $\Omega_{ed}$  is shaded by the Na concentration and  $\Omega_{el}$  is shaded by the ratio of the local current density to the applied current density.



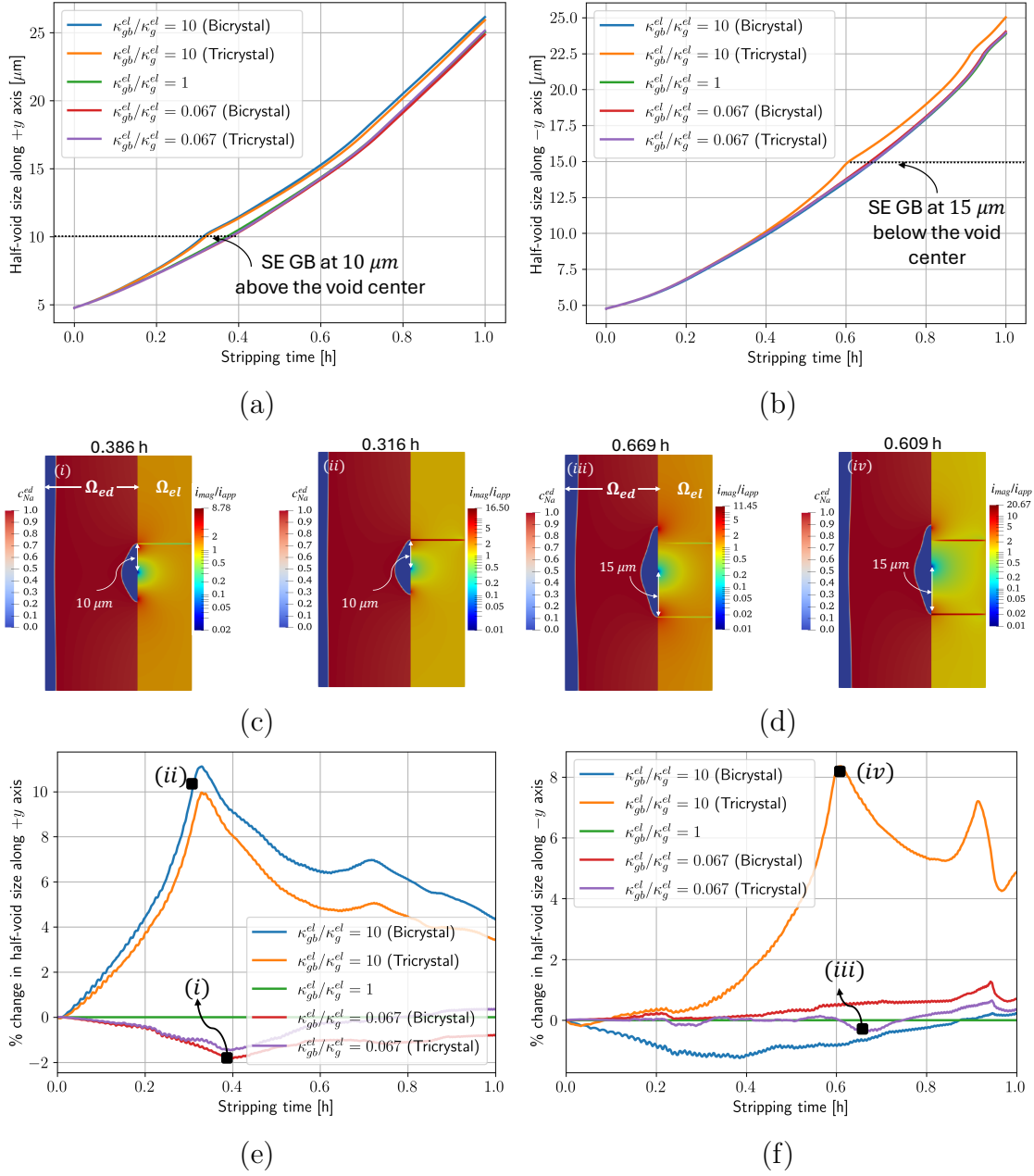
**Fig. 13.** Analysis of cycling simulations with a single interfacial void at the interface between the negative electrode and a polycrystalline SE separator. (a) Half-void size above the void center with cycling time for low-conductivity ( $\kappa_{gb}^{el}/\kappa_g^{el} = 0.067$ ), homogeneous ( $\kappa_{gb}^{el}/\kappa_g^{el} = 1.0$ ), and high-conductivity ( $\kappa_{gb}^{el}/\kappa_g^{el} = 10$ ) GBs. The black markers labelled as (i)–(iv) correspond to the microstructures shown in Fig. 12a. (b) Percentage change in upper half-void size relative to the homogeneous SE as a function of stripping time for  $\kappa_{gb}^{el}/\kappa_g^{el} = 0.067$ , 1 and 10. In (b), the black markers labelled (v)–(viii) correspond to the microstructures shown in Figs. 13c and 13d and the peaks and troughs correspond to the instances when the void edge interacts with a SE GB. Zoomed-in image of the simulation domain when the void edge touches a SE GB at a distance of (c) 6.2  $\mu\text{m}$  and (d) 16.5  $\mu\text{m}$  above the void centre. (e) The magnitude of the normalized Na flux along the electrode/electrolyte interface after stripping for 0.6 h for  $\kappa_{gb}^{el}/\kappa_g^{el} = 0.067$ , 1 and 10. In (e), the black dotted vertical line indicates the position of a SE GB at a distance of 16.5  $\mu\text{m}$  above the void center. (f) Void edge velocity using Eq. (19) with time for different GB-to-grain conductivity ratios. In (f), the solid lines indicate the moving average value of the last 15 time steps and the markers (v)–(viii) correspond to the microstructures in (c) and (d).

electrode/electrolyte interface, as depicted by the instances in Figs. 13c and 13d. More specifically, the nonuniform flux distribution due to differences in GB conductivity impacts the void growth behaviour along the electrode/electrolyte interface. Figure 13e shows that the flux near the SE GB, located at a distance of  $16.5 \mu\text{m}$  from the void center, is high in the presence of high conductivity GB and low in the presence of low conductivity GB, in comparison to the homogeneous case. This difference in the magnitude of flux near the SE GB causes differences in the void edge velocity. To verify this, the void edge velocity was calculated over time using Eq. (19) and is plotted in Fig. 13f. Two instances when the void edge velocity jumps in the presence of high-conductivity SE GB compared to the homogeneous SE case are marked with labels (vi) and (viii) in Fig. 13f. The difference in void edge velocity is relatively less in the presence of low-conductivity SE GB as compared to the homogeneous SE case. This indicates that the magnitude of the deviation in the void edge velocity depends on the relative difference in the magnitude of local flux near the SE GB compared to the homogeneous SE case. The lower void edge also interacts with SE GBs along the negative  $y$  axis as the void elongates during stripping, as shown in Fig. S6 of the Supporting Information. Moreover, Section S.12 of the Supporting Information demonstrates that the void growth is marginally asymmetric in the homogeneous SE case, and this asymmetry marginally varies with GB conductivity.

To further support our argument that GB conductivity locally affects void evolution, we have simulated the growth of a single void in contact with bicrystal and tricrystal SEs during stripping under an applied current density of  $0.5 \text{ mA/cm}^2$ . The initial conditions and the SE GB-to-grain conductivity ratios are the same as in the polycrystalline SE cases. In the bicrystal SE cases, a horizontal GB is placed at a distance of  $10 \mu\text{m}$  above the center of the void, as illustrated in Fig. 14c. On the other hand, in the tricrystal SE cases, two horizontal GBs are placed at a distance of  $10 \mu\text{m}$  above and  $15 \mu\text{m}$  below the center of the void, respectively, as illustrated in Fig. 14d.

Figures 14a and 14b show the half-void size along the positive and negative  $y$ -axes as a function of the stripping time in the case of bicrystal and tricrystal SEs with low-conductivity and high-conductivity GBs. The case with homogeneous SE (green curve) is also shown in these figures. As expected, the void edge grows along the electrode/electrolyte interface during stripping in all cases. However, the rate at which the void edge grows depends slightly on the SE GB conductivities. To quantify this, we calculated the percentage change in half-void size relative to the homogeneous SE case along both positive and negative  $y$ -axes. Figure 14e shows that the percentage change in half-void size along the  $+y$ -axis reaches a maximum value of approximately 10% and 9% in the cases of bicrystal and tricrystal





**Fig. 14.** Stripping simulations with a single interfacial void located at the interface between the negative electrode and bicrystal and tricrystal SEs under an applied current density of 0.5 mA/cm<sup>2</sup>. Temporal variation in the half-void size along the (a) positive and (b) negative  $y$ -axes for SEs with low-conductivity ( $\kappa_{gb}^{el}/\kappa_g^{el} = 0.067$ ), homogeneous ( $\kappa_{gb}^{el}/\kappa_g^{el} = 1$ ) and high-conductivity ( $\kappa_{gb}^{el}/\kappa_g^{el} = 10$ ) grain boundaries (GBs). In (a) and (b), the dotted black lines indicate the positions of the SE GBs located 10  $\mu\text{m}$  above and 15  $\mu\text{m}$  below the center of the void, respectively. Snapshots of the simulation domain as the void edge touches the SE GB positioned (c) 10  $\mu\text{m}$  above and (d) 15  $\mu\text{m}$  below the center of the void. In (c) and (d),  $\Omega_{ed}$  is shaded by the Na concentration and  $\Omega_{el}$  by the normalized current density. Temporal variation in the percentage change in half-void size along the (e) positive and (f) negative  $y$ -axes relative to the homogeneous SE case for  $\kappa_{gb}^{el}/\kappa_g^{el} = 0.067$ , 1 and 10. In (e) and (f), the black markers labelled (i)–(iv) correspond to the microstructures shown in (c) and (d).

SEs with high-conductivity GBs. These peaks correspond to the instances when the upper void edge touches the high-conductivity SE GB at a distance of  $10\text{ }\mu\text{m}$  above the center of the void (Fig. 14c (ii)). Similarly, the percentage change in half-void size along the negative  $y$ -axis reaches a maximum value of approximately 8% when the lower void edge interacts with the high-conductivity SE GB, located  $15\text{ }\mu\text{m}$  below the center of the void (Fig. 14d (iv)).

In contrast, the percentage change in half-void size along the  $+y$ -axis drops to 2% for bicrystal and tricrystal SEs with low-conductivity GBs, as indicated by label (i) in Fig. 14e. This corresponds to the instance when the upper void edge touches the low-conductivity SE GB, located  $10\text{ }\mu\text{m}$  above the center of the void (Fig. 14c (i)). In the tricrystal SE case, a similar drop is evident when the lower void edge touches the low-conductivity SE GB, positioned  $15\text{ }\mu\text{m}$  below the center of the void, as indicated by label (iii) in Fig. 14f. As previously noted, a decrease in the slope of the percentage change plot in the low-conductivity GB case suggests a slower void migration rate relative to that of the homogeneous SE case. Thus, these cases corroborate that the impact of GB conductivity on void migration rate is marginal because the percentage change in void size relative to the homogeneous case is  $\leq 10\%$ .

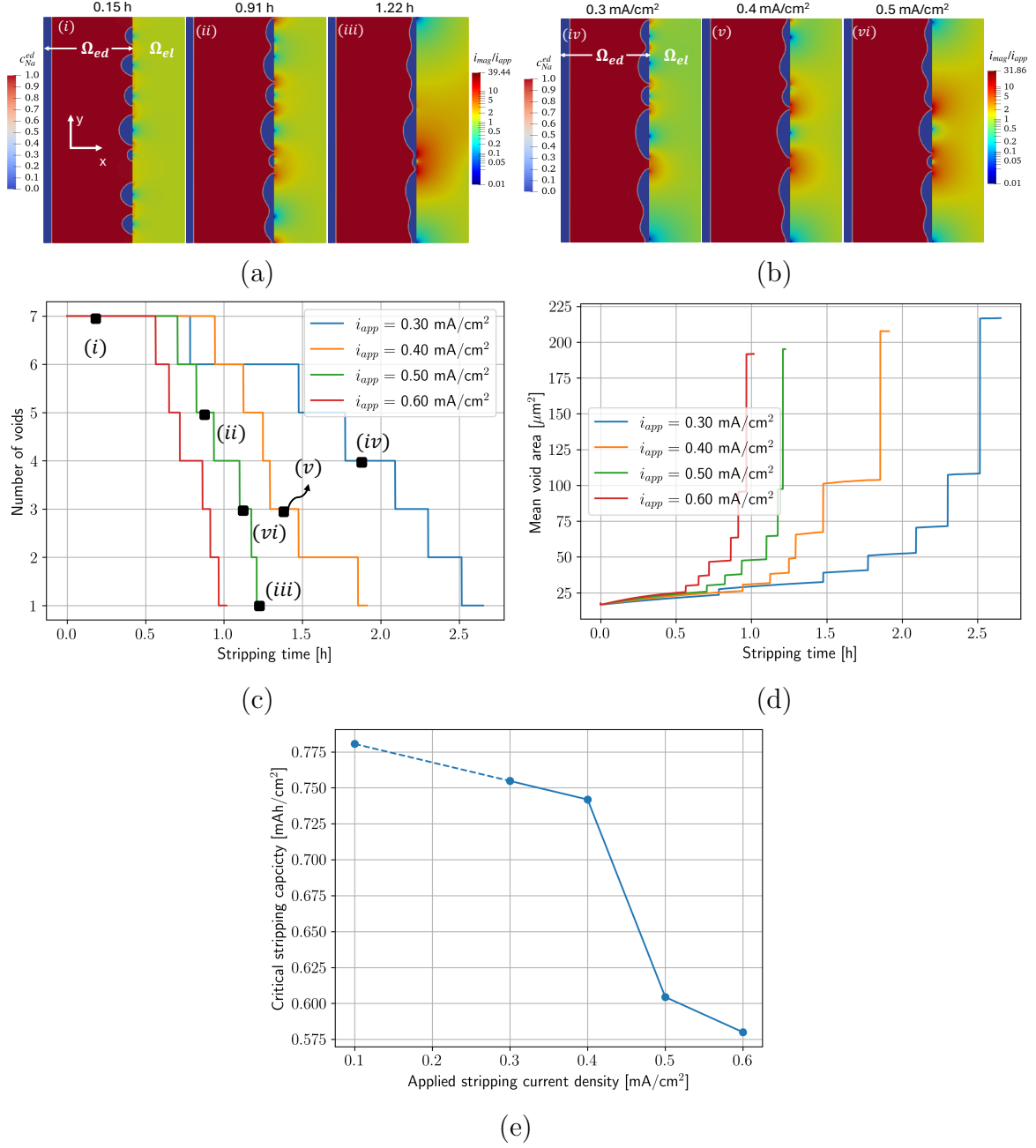
### 4.3. Multiple voids at the electrode/solid electrolyte interface

#### 4.3.1. Stripping simulations with a homogeneous solid electrolyte (SE)

It has been experimentally observed [19, 28] that contact loss between the electrode and SE during cycling occurs due to the growth, accumulation and coalescence of multiple interfacial voids. So, we investigate the time to contact loss and the coalescence rate in simulations of multiple interfacial voids during stripping. Similar to Zhao *et al.* [36], we initialize our simulations with seven semi-circular-shaped voids of different radii at the electrode/electrolyte interface, as shown in Fig. 15a. We assume an initial negative electrode thickness of  $28.6\text{ }\mu\text{m}$ . The simulations run until complete contact loss occurs between the electrode and the SE separator.

Figure 15a shows the evolution of interfacial voids during stripping with an applied current density of  $0.5\text{ mA/cm}^2$ . As stripping progresses, the void area increases while the number of voids decreases due to coalescence until complete contact loss occurs. Multiple current hot spots develop in the SE separator near the void edges with increasing contact loss. Once complete contact loss occurs the flux of  $\text{Na}/\text{Na}^+$  leaving the electrode/electrolyte interface becomes effectively zero, which hinders further shrinkage of the negative electrode.

The applied current density directly impacts the void coalescence rate during stripping. Figure 15b compares the void morphology after stripping to the same capacity,  $0.55\text{ mAh/cm}^2$ . Although the



**Fig. 15.** Stripping simulations with multiple interfacial voids at the electrode/electrolyte interface and a homogeneous solid electrolyte separator for different applied current densities. (a) Void morphology at three times with an applied current density of **0.5 mA/cm²**.  $\Omega_{ed}$  is shaded by the Na concentration and  $\Omega_{el}$  by the normalized current density. (b) Void morphology after stripping to the same capacity of 0.55 mAh/cm² with different applied current densities. Variation with time in the (c) number of voids and (d) mean void area. In (c), the black markers labelled (i)–(vi) correspond to the microstructures shown in (a) and (b). (d) Critical stripping capacity as a function of applied current density.

voids appear qualitatively similar after stripping to the same capacity, fewer voids have coalesced in the case of  $0.3 \text{ mA/cm}^2$  as compared to  $0.4 \text{ mA/cm}^2$  and  $0.5 \text{ mA/cm}^2$  (Fig. 15b), indicating that the coalescence rate increases with applied current density.

To quantify the coalescence rate, we calculate the number of voids and the mean void area, i.e., the total void area divided by the number of voids, as a function of time, as shown in Figs. 15c and 15d, respectively. The decrease in the number of voids due to coalescence accelerates with increasing applied current density, and the growth of the void area increases with increasing applied current density. Thus, the time to complete contact loss decreases with increasing applied current density. To quantify this, following Agier *et al.* [35], we calculate the critical stripping capacity  $C_{crit} = i_{app}t_f$ , which is the product of applied current density and the time to contact loss  $t_f$ . Precisely, the time to contact loss is defined as the onset time when only a single void remains in the simulation domain. The critical stripping capacity decreases with increasing applied current density, which is in qualitative agreement with experiments [29] and simulations in Li/LLZO systems [35, 37]. To compare with the experimentally measured critical stripping capacity at  $0.1 \text{ mA/cm}^2$  [29] [37], we linearly extrapolate these data to  $0.1 \text{ mA/cm}^2$ . The extrapolated data are shown as a dotted line in Fig. 15e. The predicted critical stripping capacity is about 22% lower compared to the measured critical cell capacity, which is generally around  $\sim 1 \text{ mAh/cm}^2$  for a Li/LLZO system when operated under a stack pressure of  $0.7 \text{ MPa}$  and an applied current density of  $0.1 \text{ mA/cm}^2$  [29], [37]. Note that due to the higher diffusivity of  $\text{Na}^+$  compared to  $\text{Li}^+$  in the solid electrolyte, the critical stripping capacity should be even higher in the former than in the latter. Two reasons for this discrepancy are that i) our simulations begin with voids already present at the interface, meaning that we have effectively skipped past cycles during which voids nucleated at the interface, and ii) our model does not consider the effect of the stack pressure, which suppresses void growth and thus increases the time to failure. Another factor that could explain this discrepancy is the effect of surface diffusion on void growth, which was not considered in our model.

#### 4.3.2. Stripping simulations with a polycrystalline solid electrolyte (SE)

Finally, we perform simulations to investigate the role of SE GBs on void coalescence. The initial void radii and the electrode thickness are identical to Section 4.3.1. The only difference is that we include polycrystalline SEs with low-conductivity and high-conductivity GBs instead of a homogeneous SE, as in Section 4.2.2. The simulations are performed under a fixed applied current density of  $0.5 \text{ mA/cm}^2$  and run until complete contact loss occurs between the electrode and the SE. For discussion

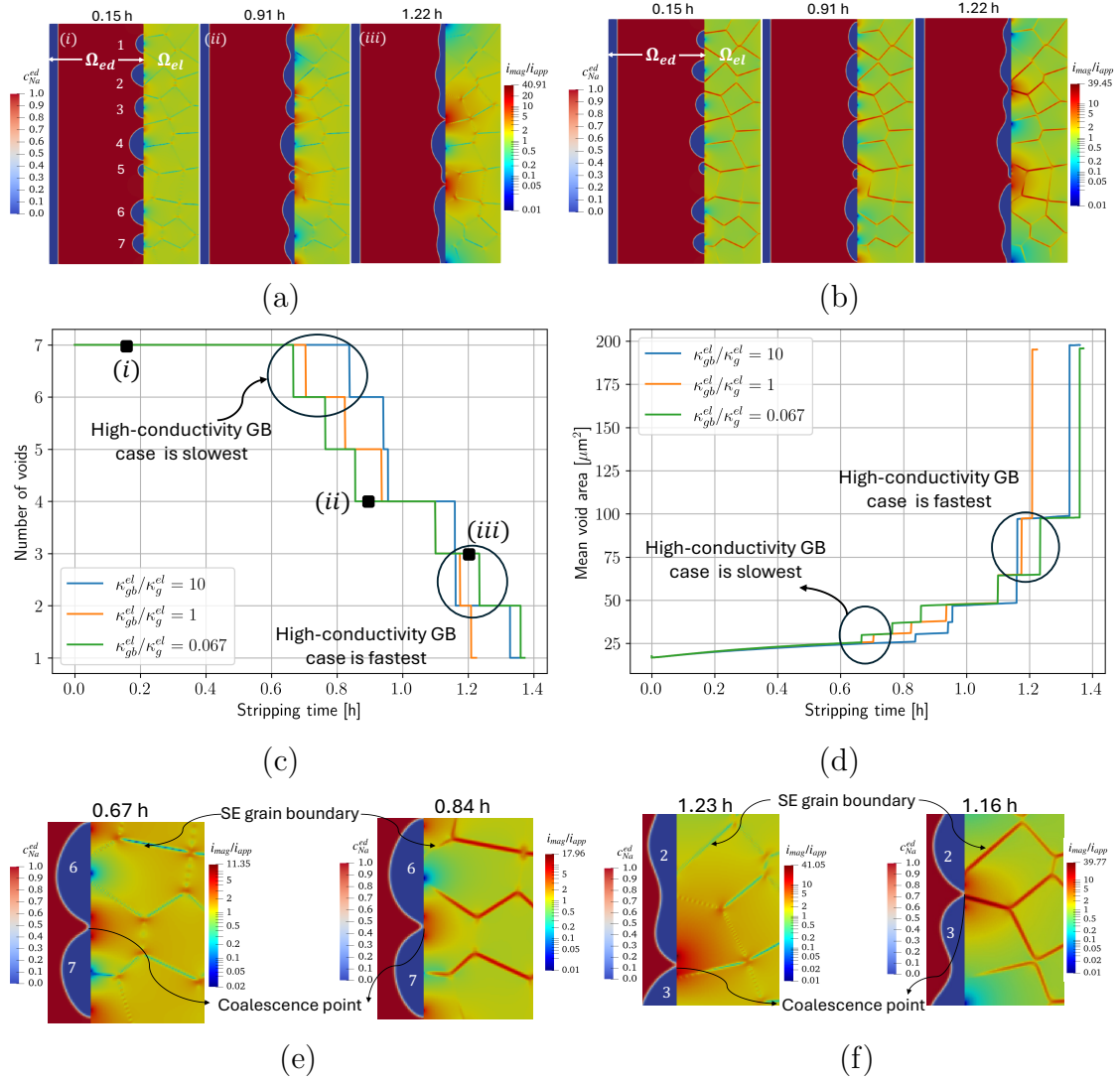
purposes, we have labelled the voids as 1 to 7 starting from the top to bottom, as shown in Fig. 16a.

Figures 16a and 16b show the evolution of interfacial voids during stripping in the case of SEs with low-conductivity and high-conductivity GBs, respectively. The void morphologies are almost identical, indicating that GB conductivities only have small effects on the void evolution. Similar to Section 4.3.1, multiple current density hot spots occur in the SE separator near the void edges due to contact loss. We again plot the number of voids and the mean void area versus time, as shown in Figs. 16c and 16d. There are noticeable differences in the void coalescence times between the low-conductivity, homogeneous, and high-conductivity GB cases.

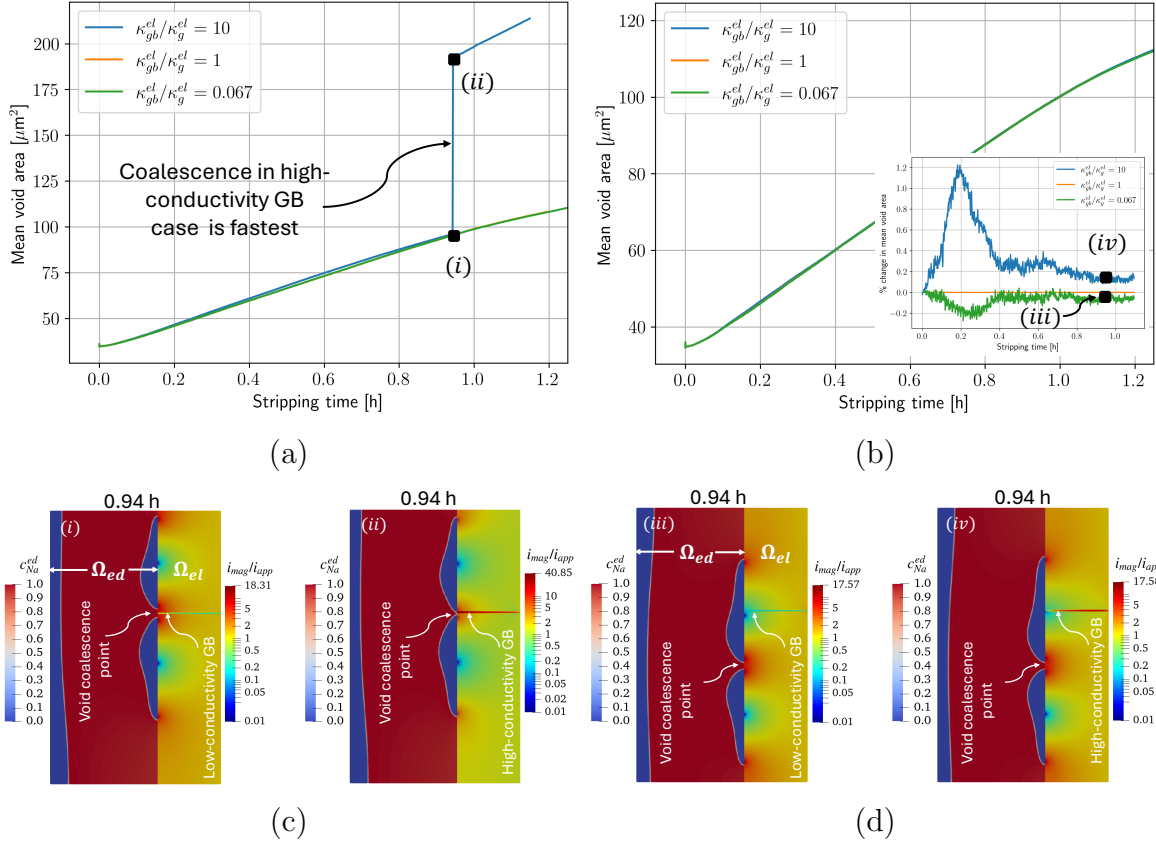
We believe the time to coalescence depends on the location at which the voids coalesce relative to the intersecting SE GB along the electrode/electrolyte interface. If the location of void coalescence lies near a SE GB, as in the case of the coalescence of voids 2 and 3 (Fig. 16f), then the coalescence rate is faster with high-conductivity GBs. This is because the void edge velocity is faster near a high-conductivity GB, as shown in Section 4.2.2. If the location of void coalescence lies away from a SE GB, as in the case of the coalescence of voids 6 and 7 (Fig. 16e), then the coalescence rate is faster in the case of low-conductivity SE separators than in homogeneous and high-conductivity SE separators.

To support our assertion that SE GB conductivity marginally affects void coalescence, we performed additional simulations involving two interfacial voids, with their centers located at the electrode/SE interface. Bicrystal SEs with both low-conductivity and high-conductivity GBs are considered under an applied stripping current density of  $0.5 \text{ mA/cm}^2$ . The voids are initially semi-circular with a radius of  $4.8 \text{ }\mu\text{m}$ . Two scenarios are simulated. In the first scenario, voids are placed such that their point of coalesce is near a SE GB, as illustrated in Fig. 17c. In the second scenario, voids are placed such that their point of coalesce is away from the SE GB, as illustrated in Fig. 17d. The centers of the voids are  $20 \text{ }\mu\text{m}$  and  $15.8 \text{ }\mu\text{m}$  apart in the first and second scenarios, respectively.

Figure 17a shows the mean void area as a function of the stripping time for different GB-to-grain conductivity ratios in the first scenario, i.e., when the SE GB is located near the coalescence point of the voids. The sharp increase in the mean void area demonstrates that voids near a high-conductivity GB coalesce after stripping for  $0.94 \text{ h}$  (Fig. 17a). On the other hand, voids near a low-conductivity GB and in the homogeneous SE case remain unconnected even after stripping for  $1.2 \text{ h}$ , as evidenced by the absence of a sharp increase in the mean void area (Fig. 17a). Figure 17c illustrates that voids near a high-conductivity SE GB have coalesced after stripping for  $0.94 \text{ h}$ , whereas voids remain unconnected near a low-conductivity GB. Moreover, the void shapes are slightly asymmetric as they prefer to grow



**Fig. 16.** Stripping simulations with an applied current density of  $0.5 \text{ mA/cm}^2$ , multiple interfacial voids, and a polycrystalline SE separator with different values of  $\kappa_{gb}^{el}/\kappa_g^{el}$ . Void morphology at three times with (a) low-conductivity and (b) high-conductivity GBs. The initial voids are numbered in (a).  $\Omega_{ed}$  is shaded by the Na concentration and  $\Omega_{el}$  by the normalized current density. Variation with time of the (c) number of voids and (d) mean void area. In (c), the black markers labelled (i) – (iii) correspond to the microstructures shown in (a). Zoomed-in image of void morphologies when (e) voids 6 and 7 and (f) and 2 and 3 coalesce.



**Fig. 17.** Stripping simulations involving two interfacial voids and a bicrystal solid electrolyte (SE) separator under an applied current density of  $0.5 \text{ mA/cm}^2$ . Temporal variation in the mean void area when a SE GB is located (a) near and (b) away from the coalescence point of voids. In (b), the inset shows the temporal variation in the percentage change in the mean void area relative to the homogeneous SE case ( $\kappa_{gb}^{el}/\kappa_g^{el} = 1$ ). In (a) and (b), the black markers labelled (i)–(iv) correspond to the microstructures shown in (c) and (d). Simulation domains after stripping for 0.94 h in the case when a SE GB is located (c) near and (d) away from the coalescence point of voids. In (c) and (d),  $\Omega_{ed}$  is shaded by the Na concentration and  $\Omega_{el}$  is shaded by the ratio of the local current density to the applied current density.

away from the point of coalescence. This shows that voids near high-conductivity GBs tend to coalesce faster compared to voids near low-conductivity GBs because void migration becomes marginally faster in the presence of high-conductivity SE GBs, as discussed in Section 4.2.2.

In contrast, in the second scenario, the voids remain unconnected in all cases even after stripping for 1.2 h, as evidenced by the absence of a sharp increase in the mean void area (Fig. 17b). Fig. 17d shows that voids prefer to grow away from the point of coalescence instead of towards it, regardless of the GB conductivity. This result shows that the void coalescence behaviour depends on the position of the SE GB relative to the point of coalescence. Nonetheless, on closer inspection, it is observed that the SE GB does slightly affect the rate of change in the mean void area in the second scenario. To quantify this, we calculated the percentage change in the mean void area relative to the homogeneous case over time. As the inset in Fig. 17b shows, the percentage change in the mean void area increases to a maximum value of 1.2% at around 0.2 h in the high-conductivity SE case. In contrast, it decreases by 0.2% in the low-conductivity SE case after stripping for about 0.2 h. These deviations in the mean void area occur due to the marginal impact of GB conductivity on the void evolution rate.

## 5. Conclusions

We have presented an electrochemical phase-field model to simulate the evolution of a metallic negative electrode during the stripping and plating of an all-solid-state battery, first assuming a perfect contact between the electrode and the solid-electrolyte separator. We extended this model to simultaneously simulate the evolution of single and multiple interfacial voids at the electrode/solid-electrolyte separator interface during stripping and plating. The model was numerically solved using the finite-element method. For the first time, the stripping and plating processes in a solid-state cell with a metallic Na electrode in contact with a Na- $\beta''$ -alumina (NBA) ceramic solid electrolyte separator were simulated. Nonetheless, it is essential to note that, while our model has been applied to Na-metal solid-state batteries (SSBs), it is equally applicable for simulating electrode and/or void evolution during stripping/plating in Li-metal SSBs.

Both homogeneous and polycrystalline solid electrolytes were considered in this work. We demonstrated the impact of applied current density on electrode deposition/depletion and void edge velocities. The unique contribution of this work compared to previous works [35–37, 45, 46] is that the role of the solid electrolyte grain boundary properties on deposition/depletion rates and void edge migration rates were directly considered. Our results show that:



- The Na negative electrode shrinks and grows during stripping and plating, respectively. The depletion and deposition rates are proportional to the applied current density and consistent with sharp-interface electrochemical models [44], assuming a perfect electrode/electrolyte interface.
- In cases with a perfect electrode/electrolyte interface, the thickness of the Na electrode exhibits a slight curvature during cycling in both SEs with low-conductivity and high-conductivity GBs owing to the non-uniform flux distribution along the electrode/electrolyte interface, as opposed to the homogeneous SE case.
- Interfacial voids preferentially grow and shrink along the electrode/electrolyte interface during stripping and plating. Their migration rate is proportional to the flux of Na/Na<sup>+</sup> at the void edge, which depends on the applied current density. These voids block the shrinkage and growth of the Na-negative electrode during stripping and plating.
- SE GB properties impact the local interfacial void migration rate and the void coalescence rate, though the effect is small.

Though this work has made significant progress in modeling solid-state Na batteries, additional work is needed. First, the charge-transfer kinetics at the electrode/electrolyte interface are currently ignored but should be included in the future model. Second, the effect of applied stack pressure on void growth should be incorporated into this model. Third, multiple charge/discharge cycles should be simulated to predict cell failure accurately. Although we have presented only 2D results, our model can be readily extended to 3D, as MOOSE is inherently dimension-agnostic [69]. A 3D simulation is particularly relevant when comparing computational predictions with experimental data. For instance, in the experimental study of void formation in a Na/Na- $\beta''$ -alumina cell [28], the authors reported the number of voids and the total void volume with cycle number. To make a quantitative comparison with such data, it is essential to perform 3D simulations, as even initializing with so many voids while having comparable volume ranges as in experiments, is impractical in a two-dimensional domain.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgements

This work was funded by a subcontract from the company QuantumScape. The authors would like to thank Chaitanya Bhawe for his initial work modeling batteries with his electrochemical phase-field model developed for molten salt corrosion. Part of this work was performed under the auspices of the US Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 (Sourav Chatterjee)

## Data Availability

The data that support the findings of this study are available from the corresponding authors (SC and MT) upon reasonable request. The MOOSE-based input files and the source code are publicly available via the GitHub repository at <https://github.com/souravmat-git/MOOSE-BatModelling.git>.

## Appendix A

### A.1. Reduction of Eq. (6) to Fick's law

It is important to note that in a grand-potential-based formulation, the overall concentration is a function of the phase-field variables and the diffusion potential of the species. This is because by definition,  $c_M^{ed}(\{\xi\}, \mu_M^{ed}) = -\delta\Psi/\delta\mu_M^{ed}$ , where  $\{\xi\}$  represents the set of three phase-field variables  $\xi_a$ ,  $\xi_m$  and  $\xi_v$ . Consequently, its gradient may be written as:

$$\nabla c_M^{ed} = \sum_{p=a,m,v} \frac{\partial c_M^{ed}}{\partial \xi_p} \nabla \xi_p + \frac{\partial c_M^{ed}}{\partial \mu_M^{ed}} \nabla \mu_M^{ed}. \quad (\text{A.1})$$

Moreover, using the definition of  $c_M^{ed}$  and Eq. (1), it follows that

$$c_M^{ed}(\{\xi\}, \mu_M^{ed}) = \sum_{p=a,m,v} h_p^{ed} c_M^p, \quad (\text{A.2})$$

where we have used the relation  $c_M^p = -\partial\omega_p/\partial\mu_M^{ed}$  that follows from Eq. (3). Using Eq. (A.2), Eq. (A.1) may be equivalently written as:

$$\nabla c_M^{ed} = \sum_{p=a,m,v} \left( \sum_{r=a,m,v} \frac{\partial h_r^{ed}}{\partial \xi_p} c_M^r \right) \nabla \xi_p + \frac{\partial c_M^{ed}}{\partial \mu_M^{ed}} \nabla \mu_M^{ed}. \quad (\text{A.3})$$

Note that the first term in Eq. (A.3) vanishes in the bulk regions of the phases since  $\nabla \xi_p = 0$  and  $\partial h_r^{ed}/\partial \xi_p = 0$ . We can, therefore, say that in the bulk regions  $\nabla c_M^{ed}|_{\xi_p=1} = (\partial c_M^{ed}/\partial \mu_M^{ed}) \nabla \mu_M^{ed}$ , where the subscript  $\xi_p = 1$  indicates the bulk regions of either the auxiliary phase, metallic negative electrode or the void phase. Thus, using  $M_p = D_M^p dc_M^p/d\mu_M^{ed}$ , Eq. (6) in the bulk regions reduces to:

$$j_M^{ed}|_{\xi_p=1} = -\frac{D_M^p}{v_m} \nabla c_M^{ed}|_{\xi_p=1}, \quad p = a, m, v. \quad (\text{A.4})$$

### A.2. Derivation of Eq. (8)

To derive Eq. (8), we start by taking the time derivative of Eq. (A.2). This yields:

$$\frac{\partial c_M^{ed}}{\partial t} = \sum_{p=a,m,v} \frac{\partial h_p}{\partial t} c_M^p + \sum_{p=a,m,v} h_p \frac{\partial c_M^p}{\partial t}. \quad (\text{A.5})$$

Further, it can be shown that:

$$\frac{\partial h_p}{\partial t} = \sum_{q=a,m,v} \frac{\partial h_p}{\partial \xi_q} \frac{\partial \xi_q}{\partial t} \quad (\text{A.6})$$

$$\frac{\partial c_M^p}{\partial t} = \frac{\partial c_M^p}{\partial \mu_M^{ed}} \frac{\partial \mu_M^{ed}}{\partial t}. \quad (\text{A.7})$$

Substituting Eqs. (A.6) and (A.7) in (A.5) yields:

$$\frac{\partial c_M^{ed}}{\partial t} = \sum_{p=a,m,v} \left( \sum_{q=a,m,v} \frac{\partial h_p}{\partial \xi_q} \frac{\partial \xi_q}{\partial t} \right) c_M^p + \sum_{p=a,m,v} h_p \frac{\partial c_M^p}{\partial \mu_M^{ed}} \frac{\partial \mu_M^{ed}}{\partial t}. \quad (\text{A.8})$$

Using Eq. (6) in Eq. A.5 yields Eq. (8), i.e.,

$$\left[ \sum_{\substack{p= \\ a,m,v}} \frac{h_p}{v_m} \frac{\partial c_M^p}{\partial \mu_M^{ed}} \right] \frac{\partial \mu_M^{ed}}{\partial t} + \nabla J_M^{ed} + \sum_{\substack{p= \\ a,m,v}} \left( \sum_{q=a,m,v} \frac{\partial h_p}{\partial \xi_q} \frac{\partial \xi_q}{\partial t} \right) \frac{c_M^p}{v_m} = 0. \quad (\text{A.9})$$

### A.3. Non-dimensionalization of the governing equations

This section provides the non-dimensional form of the governing equations assuming Na is the diffusing species in the auxiliary-electrode-void region, i.e.,  $\Omega_{ed}$ . For numerical convergence reasons, we scale the gradient operator, time, energy density and the field variables as follows:

$$\tilde{\nabla} = \nabla l_c, \quad \tilde{t} = \frac{t}{\tau}, \quad \tilde{\omega}_p = \frac{\omega_p}{f_c}, \quad \tilde{\mu}_{Na}^{ed} = \frac{\mu_{Na}^{ed}}{RT}, \quad \tilde{\phi}^{el} = \frac{F\phi^{el}}{RT}, \quad \tilde{\phi}^{ed} = \frac{F\phi^{ed}}{RT}, \quad (\text{A.10})$$

where tilde ( $\tilde{\cdot}$ ) indicates a non-dimensional quantity;  $l_c$  is a characteristic length;  $\tau$  is a characteristic time;  $R$  is universal gas constant,  $T$  is temperature;  $F$  is Faraday constant; and  $f_c$  is characteristic energy density. For our simulations, we assumed  $\tau = l_c^2/D_{Na}^m$  and  $f_c = RT/v_m$ . These parameters are listed in Table 1. Using the variables in Eq. (A.10), Eq. (5) may be written as:

$$\frac{\partial \xi_p}{\partial \tilde{t}} + \tilde{L}_\phi \left[ \left\{ \xi_p^3 - \xi_p + 3\xi_p \sum_{\substack{q=a,m,v \\ q \neq p}} \xi_q^2 \right\} - \tilde{\kappa} \tilde{\nabla}^2 \xi_p + \frac{f_c}{m} \sum_{q=a,m,v} \frac{\partial h_q^{ed}}{\partial \xi_p} \tilde{\omega}_q \right] = 0 \quad p = a, m, v, \quad \text{in } \Omega_{ed}, \quad (\text{A.11})$$

where  $\tilde{L}_\phi = L_\phi \tau m$  and  $\tilde{\kappa} = \kappa / (m l_c^2)$ . It should be noted that the dimensionless grand potential densities in Eq. (A.11) are related to Eq. (S.3) via:

$$\tilde{\omega}_p(\tilde{\mu}_{Na}^{ed}) = - \left[ \frac{(\tilde{\mu}_{Na}^{ed})^2}{\tilde{A}^p} + \tilde{\mu}_{Na}^{ed} c_{Na}^{eq,p} \right] = \frac{\omega_p}{f_c} \quad p = a, m, v \quad \text{in} \quad \Omega_{ed}, \quad (\text{A.12})$$

where  $\tilde{A}^p = A^p / f_c$  for  $p = \{a, m, v\}$  denote the non-dimensional parabolic coefficients of the auxiliary phase, negative electrode and void. These values are provided in Table 1. Similarly, substituting Eq. (6) in Eq. (8) and using the variables in Eq. (A.10) yields:

$$\begin{aligned} & \left[ \sum_{\substack{p=a, m, v \\ p=}} \frac{dc_{Na}^p}{d\tilde{\mu}_{Na}^{ed}} h_p^{ed} \right] \frac{\partial \tilde{\mu}_{Na}^{ed}}{\partial t} - \tilde{\nabla} \left( h_a^{ed} \tilde{M}_a + h_m^{ed} \tilde{M}_m + h_v^{ed} \tilde{M}_v \right) \tilde{\nabla} \tilde{\mu}_{Na}^{ed} \\ & + \sum_{\substack{p=a, m, v \\ p=}} \left( \sum_{q=a, m, v} \frac{\partial h_p}{\partial \xi_q} \frac{\partial \xi_q}{\partial t} \right) c_{Na}^p = 0 \quad \text{in} \quad \Omega_{ed}, \end{aligned} \quad (\text{A.13})$$

where  $\tilde{M}_p = (M_p \tau RT) / l_c^2$  for  $p = \{a, m, v\}$  denote the non-dimensional mobilities in the auxiliary phase, negative electrode and void. The phase mole fractions of Na in these phases, which are required in Eq. (A.13), are obtained from Eq. (S.2) and can be written in a non-dimensional form as

$$c_{Na}^p(\tilde{\mu}_{Na}^{ed}) = \frac{\tilde{\mu}_{Na}^{ed}}{\tilde{A}^p} + c_{Na}^{eq,p} \quad p = a, m, v \quad \text{in} \quad \Omega_{ed}. \quad (\text{A.14})$$

Using Eqn (A.14), the inverse of thermodynamic factors, which are required in Eq. (A.13), can be written in a non-dimensional form according to

$$\frac{dc_{Na}^p}{d\tilde{\mu}_{Na}^{ed}} = \frac{1}{\tilde{A}^p} \quad p = a, m, v \quad \text{in} \quad \Omega_{ed}. \quad (\text{A.15})$$

Likewise, substituting Eq. (9) in Eq. (10) and using the variables in Eq. (A.10) yields:

$$-\tilde{\nabla} \left[ (\tilde{\sigma}_a h_a^{ed} + \tilde{\sigma}_m h_m^{ed} + \tilde{\sigma}_v h_v^{ed}) \tilde{\nabla} \tilde{\phi}^{ed} \right] = 0 \quad \text{in} \quad \Omega_{ed}, \quad (\text{A.16})$$

where  $\tilde{\sigma}_p = (\sigma_p RT \tau v_m) / (F^2 l_c^2)$  for  $p = \{a, m, v\}$  denote the non-dimensional electronic conductivities of the auxiliary phase, negative electrode and void.

Following a similar procedure, we can obtain the non-dimensional form of the equations in the

region  $\Omega_{el}$ . Specifically, combining Eq. (11) with Eq. (12) yields:

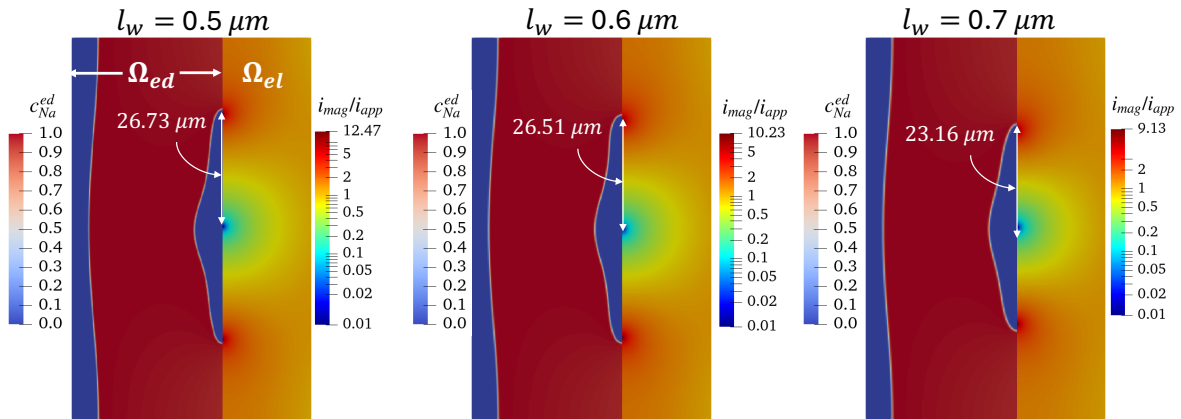
$$-\tilde{\nabla} \left[ \{ \tilde{\kappa}_g^{el} (h_g^{el} - h_{gb}^{el}) + \tilde{\kappa}_{gb}^{el} h_{gb}^{el} \} \tilde{\nabla} \tilde{\phi}^{el} \right] = 0 \quad \text{in } \Omega_{el}, \quad (\text{A.17})$$

where  $\tilde{\kappa}_p^{el} = (\kappa_p^{el} RT \tau v_m) / (F^2 l_c^2)$  for  $p = \{g, gb\}$  are the non-dimensional ionic conductivities of the solid electrolyte grains and grain boundaries.

#### A.4. Influence of interface width on single interfacial void simulations

This section demonstrates the sensitivity of void size and current density to variations in the width of the diffuse interface. Specifically, the growth of a single interfacial void in contact with a homogeneous solid electrolyte during stripping is simulated for three different diffuse interface widths,  $l_w$ . As in Section 4.2.1, the initial void radius is  $4.8 \mu\text{m}$  and the void center is located at the electrode/electrolyte interface. The applied current density is  $0.5 \text{ mA/cm}^2$  in all cases.

Figure A.1 shows the morphology of the void after stripping for 1 h with three different interface widths. The void shape and the current density distribution within the solid electrolyte exhibit qualitative similarities in all cases. However, the maximum value of the magnitude of the current density near the void edges decreases as the width of the interface increases. This indicates that the magnitude of flux concentration near the void edge decreases with interface width for a given applied current density. In Section 4.2.1, it was demonstrated that the rate of void growth depends on the magnitude of flux concentration near the void edges. Consequently, the void size decreases with increasing interface width, as shown in Fig. A.1.



**Fig. A.1.** Simulation domain with a single interfacial void at the electrode/electrolyte interface and a homogeneous solid electrolyte separator after stripping for 1 h under an applied current density of  $0.5 \text{ mA/cm}^2$  with different interface widths,  $l_w$ .  $\Omega_{ed}$  is shaded by the Na concentration and  $\Omega_{el}$  is shaded by the ratio of the local current density to the applied current density.

## References

- [1] K. Takada, Progress and prospective of solid-state lithium batteries, *Acta Materialia* 61 (3) (2013) 759–770.
- [2] B. Wang, X.-Y. Lu, Y. Tang, W. Ben, General polyethyleneimine-mediated synthesis of ultrathin hexagonal  $\text{Co}_3\text{O}_4$  nanosheets with reactive facets for lithium-ion batteries, *ChemElectroChem* 3 (1) (2016) 55–65.
- [3] J. Janek, W. G. Zeier, A solid future for battery development, *Nature energy* 1 (9) (2016) 1–4.
- [4] C. Barchasz, F. Molton, C. Duboc, J.-C. Leprêtre, S. Patoux, F. Alloin, Lithium/sulfur cell discharge mechanism: an original approach for intermediate species identification, *Analytical chemistry* 84 (9) (2012) 3973–3980.
- [5] J. Liu, Z. Bao, Y. Cui, E. J. Dufek, J. B. Goodenough, P. Khalifah, Q. Li, B. Y. Liaw, P. Liu, A. Manthiram, et al., Pathways for practical high-energy long-cycling lithium metal batteries, *Nature Energy* 4 (3) (2019) 180–186.
- [6] X. Feng, H. Fang, N. Wu, P. Liu, P. Jena, J. Nanda, D. Mitlin, Review of modification strategies in emerging inorganic solid-state electrolytes for lithium, sodium, and potassium batteries, *Joule* 6 (3) (2022) 543–587.
- [7] K. Park, J. B. Goodenough, Dendrite-suppressed lithium plating from a liquid electrolyte via wetting of  $\text{Li}_3\text{N}$ , *Advanced Energy Materials* 7 (19) (2017) 1700732.
- [8] C. Vaalma, D. Buchholz, M. Weil, S. Passerini, A cost and resource analysis of sodium-ion batteries, *Nature reviews materials* 3 (4) (2018) 1–11.
- [9] A. Battistel, M. S. Palagonia, D. Brogioli, F. L. Mantia, R. Trócoli, Electrochemical Methods for Lithium Recovery: A Comprehensive and Critical Review, *Adv. Mater.* (2020).
- [10] C. Zhao, L. Liu, X. Qi, Y. Lu, F. Wu, J. Zhao, Y. Yu, Y.-S. Hu, L. Chen, Solid-state sodium batteries, *Advanced Energy Materials* 8 (17) (2018) 1703012.
- [11] B. Lee, E. Paek, D. Mitlin, S. W. Lee, Sodium metal anodes: emerging solutions to dendrite growth, *Chemical reviews* 119 (8) (2019) 5416–5460.

- [12] F. Han, A. S. Westover, J. Yue, X. Fan, F. Wang, M. Chi, D. N. Leonard, N. J. Dudney, H. Wang, C. Wang, High electronic conductivity as the origin of lithium dendrite formation within solid electrolytes, *Nature Energy* 4 (3) (2019) 187–196.
- [13] Y. Lu, L. Li, Q. Zhang, Z. Niu, J. Chen, Electrolyte and Interface Engineering for Solid-State Sodium Batteries, *Joule* 2 (9) (2018) 1747–1770. doi:10.1016/j.joule.2018.07.028.
- [14] E. Kazyak, R. Garcia-Mendez, W. S. LePage, A. Sharafi, A. L. Davis, A. J. Sanchez, K.-H. Chen, C. Haslam, J. Sakamoto, N. P. Dasgupta, Li penetration in ceramic solid electrolytes: operando microscopy analysis of morphology, propagation, and reversibility, *Matter* 2 (4) (2020) 1025–1048.
- [15] D. Spencer Jolly, J. Perera, S. D. Pu, D. L. Melvin, P. Adamson, P. G. Bruce, High critical currents for dendrite penetration and voiding in potassium metal anode solid-state batteries, *Journal of Solid State Electrochemistry* 26 (9) (2022) 1961–1968.
- [16] E. J. Cheng, A. Sharafi, J. Sakamoto, Intergranular li metal propagation through polycrystalline  $\text{Li}_6\text{La}_2\text{Zr}_2\text{O}_{12}$  ceramic electrolyte, *Electrochimica Acta* 223 (2017) 85–91.
- [17] A. Sharafi, C. G. Haslam, R. D. Kerns, J. Wolfenstine, J. Sakamoto, Controlling and correlating the effect of grain size with the mechanical and electrochemical properties of  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  solid-state electrolyte, *Journal of Materials Chemistry A* 5 (40) (2017) 21491–21504.
- [18] M. J. Wang, R. Choudhury, J. Sakamoto, Characterizing the li-solid-electrolyte interface dynamics as a function of stack pressure and current density, *Joule* 3 (9) (2019) 2165–2178.
- [19] J. Kasemchainan, S. Zekoll, D. Spencer Jolly, Z. Ning, G. O. Hartley, J. Marrow, P. G. Bruce, Critical stripping current leads to dendrite formation on plating in lithium anode solid electrolyte cells, *Nature materials* 18 (10) (2019) 1105–1111.
- [20] X. Ke, Y. Wang, L. Dai, C. Yuan, Cell failures of all-solid-state lithium metal batteries with inorganic solid electrolytes: Lithium dendrites, *Energy Storage Materials* 33 (2020) 309–328.
- [21] V. Raj, V. Venturi, V. R. Kankanallu, B. Kuiri, V. Viswanathan, N. P. B. Aetukuri, Direct correlation between void formation and lithium dendrite growth in solid-state electrolytes with interlayers, *Nature Materials* 21 (9) (2022) 1050–1056.



- [22] Y.-S. Hong, N. Li, H. Chen, P. Wang, W.-L. Song, D. Fang, In operando observation of chemical and mechanical stability of li and na dendrites under quasi-zero electrochemical field, *Energy Storage Materials* 11 (2018) 118–126.
- [23] M.-C. Bay, M. Wang, R. Grissa, M. V. Heinz, J. Sakamoto, C. Battaglia, Sodium plating from na- $\beta''$ -alumina ceramics at room temperature, paving the way for fast-charging all-solid-state batteries, *Advanced Energy Materials* 10 (3) (2020) 1902899.
- [24] H. Koshikawa, S. Matsuda, K. Kamiya, M. Miyayama, Y. Kubo, K. Uosaki, K. Hashimoto, S. Nakanishi, Dynamic changes in charge-transfer resistance at li metal/li<sub>7</sub>la<sub>3</sub>zr<sub>2</sub>o<sub>12</sub> interfaces during electrochemical li dissolution/deposition cycles, *Journal of power sources* 376 (2018) 147–151.
- [25] W. Manalastas Jr, J. Rikarte, R. J. Chater, R. Brugge, A. Aguadero, L. Buannic, A. Llordés, F. Aguesse, J. Kilner, Mechanical failure of garnet electrolytes during li electrodeposition observed by in-operando microscopy, *Journal of Power Sources* 412 (2019) 287–293.
- [26] D. Devaux, K. J. Harry, D. Y. Parkinson, R. Yuan, D. T. Hallinan, A. A. MacDowell, N. P. Balsara, Failure mode of lithium metal batteries with a block copolymer electrolyte analyzed by x-ray microtomography, *Journal of The Electrochemical Society* 162 (7) (2015) A1301.
- [27] T. Krauskopf, F. H. Richter, W. G. Zeier, J. Janek, Physicochemical concepts of the lithium metal anode in solid-state batteries, *Chemical reviews* 120 (15) (2020) 7745–7794.
- [28] D. Spencer Jolly, Z. Ning, J. E. Darnbrough, J. Kasemchainan, G. O. Hartley, P. Adamson, D. E. Armstrong, J. Marrow, P. G. Bruce, Sodium/na  $\beta''$  alumina interface: effect of pressure on voids, *ACS applied materials & interfaces* 12 (1) (2019) 678–685.
- [29] T. Krauskopf, H. Hartmann, W. G. Zeier, J. Janek, Toward a fundamental understanding of the lithium metal anode in solid-state batteries—an electrochemo-mechanical study on the garnet-type solid electrolyte li<sub>6</sub>.<sub>25</sub>al<sub>0.25</sub>la<sub>3</sub>zr<sub>2</sub>o<sub>12</sub>, *ACS applied materials & interfaces* 11 (15) (2019) 14463–14477.
- [30] Y. Lu, C.-Z. Zhao, J.-K. Hu, S. Sun, H. Yuan, Z.-H. Fu, X. Chen, J.-Q. Huang, M. Ouyang, Q. Zhang, The void formation behaviors in working solid-state li metal batteries, *Science Advances* 8 (45) (2022) eadd0510.

- [31] T. Krauskopf, B. Mogwitz, C. Rosenbach, W. G. Zeier, J. Janek, Diffusion limitation of lithium metal and li-mg alloy anodes on llzo type solid electrolytes as a function of temperature and pressure, *Advanced Energy Materials* 9 (44) (2019) 1902568.
- [32] R. J.-Y. Park, C. M. Eschler, C. D. Fincher, A. F. Badel, P. Guan, M. Pharr, B. W. Sheldon, W. C. Carter, V. Viswanathan, Y.-M. Chiang, Semi-solid alkali metal electrodes enabling high critical current densities in solid electrolyte batteries, *Nature Energy* 6 (3) (2021) 314–322.
- [33] M. Yang, Y. Liu, A. M. Nolan, Y. Mo, Interfacial atomistic mechanisms of lithium metal stripping and plating in solid-state batteries, *Advanced Materials* 33 (3 2021). doi:10.1002/adma.202008081.
- [34] C.-T. Yang, Y. Qi, Maintaining a flat li surface during the li stripping process via interface design, *Chemistry of Materials* 33 (8) (2021) 2814–2823.
- [35] J. Agier, S. Shishvan, N. Fleck, V. Deshpande, Void growth within li electrodes in solid electrolyte cells, *Acta Materialia* 240 (2022) 118303.
- [36] Y. Zhao, R. Wang, E. Martínez-Pañeda, A phase field electro-chemo-mechanical formulation for predicting void evolution at the li–electrolyte interface in all-solid-state batteries, *Journal of the Mechanics and Physics of Solids* 167 (2022) 104999.
- [37] P. Barai, T. Fuchs, E. Trevisanello, F. H. Richter, J. Janek, V. Srinivasan, Study of void formation at the lithium— solid electrolyte interface, *Chemistry of Materials* 36 (5) (2024) 2245–2258.
- [38] E. Milan, M. Pasta, The role of grain boundaries in solid-state li-metal batteries, *Materials Futures* 2 (1) (2022) 013501.
- [39] J. A. Dawson, P. Canepa, T. Famprikis, C. Masquelier, M. S. Islam, Atomic-scale influence of grain boundaries on li-ion conduction in solid electrolytes for all-solid-state batteries, *Journal of the American Chemical Society* 140 (1) (2018) 362–368.
- [40] S. Breuer, D. Prutsch, Q. Ma, V. Epp, F. Preishuber-Pflügl, F. Tietz, M. Wilkening, Separating bulk from grain boundary li ion conductivity in the sol–gel prepared solid electrolyte li 1.5 al 0.5 ti 1.5 (po 4) 3, *Journal of Materials Chemistry A* 3 (42) (2015) 21343–21350.
- [41] H. Yamada, D. Tsunoe, S. Shiraishi, G. Isomichi, Reduced grain boundary resistance by surface modification, *The Journal of Physical Chemistry C* 119 (10) (2015) 5412–5419.

- [42] H.-K. Tian, Z. Liu, Y. Ji, L.-Q. Chen, Y. Qi, Interfacial electronic properties dictate li dendrite growth in solid electrolytes, *Chemistry of Materials* 31 (18) (2019) 7351–7359.
- [43] K. Tantratian, H. Yan, K. Ellwood, E. T. Harrison, L. Chen, Unraveling the li penetration mechanism in polycrystalline solid electrolytes, *Advanced Energy Materials* 11 (13) (2021) 2003417.
- [44] L. Mishra, A. Subramaniam, T. Jang, K. Shah, M. Uppaluri, S. A. Roberts, V. R. Subramanian, Perspective—mass conservation in models for electrodeposition/stripping in lithium metal batteries, *Journal of The Electrochemical Society* 168 (9) (2021) 092502.
- [45] S. Narayan, L. Anand, On modeling the detrimental effects of inhomogeneous plating-and-stripping at a lithium-metal/solid-electrolyte interface in a solid-state-battery, *Journal of The Electrochemical Society* 167 (4) (2020) 040525.
- [46] T. Jang, L. Mishra, K. Shah, A. Subramaniam, M. Uppaluri, S. A. Roberts, V. R. Subramanian, Towards real-time simulation of two-dimensional models for electrodeposition/stripping in lithium-metal batteries, *ECS Transactions* 104 (1) (2021) 131.
- [47] T. Jang, L. Mishra, S. A. Roberts, B. Planden, A. Subramaniam, M. Uppaluri, D. Linder, M. P. Gururajan, J.-G. Zhang, V. R. Subramanian, Battphase—a convergent, non-oscillatory, efficient algorithm and code for predicting shape changes in lithium metal batteries using phase-field models: Part i. secondary current distribution, *Journal of The Electrochemical Society* 169 (8) (2022) 080516.
- [48] M. Plapp, Unified derivation of phase-field models for alloy solidification from a grand-potential functional, *Physical Review E* 84 (3) (2011) 031601.
- [49] A. Choudhury, B. Nestler, Grand-potential formulation for multicomponent phase transformations combined with thin-interface asymptotics of the double-obstacle potential, *Phys. Rev. E* 85 (2) (2012) 021602–1–16. doi:10.1103/PhysRevE.85.021602.  
URL <https://link.aps.org/doi/10.1103/PhysRevE.85.021602>
- [50] L. K. Aagesen, Y. Gao, D. Schwen, K. Ahmed, Grand-potential-based phase-field model for multiple phases, grains, and chemical components, *Physical Review E* 98 (2) (2018) 023309.
- [51] C. V. Bhawe, G. Zheng, K. Sridharan, D. Schwen, M. R. Tonks, An electrochemical mesoscale tool for modeling the corrosion of structural alloys by molten salt, *Journal of Nuclear Materials* 574 (2023) 154147.

- [52] S. G. Kim, W. T. Kim, T. Suzuki, Phase-field model for binary alloys, *Physical review e* 60 (6) (1999) 7186.
- [53] N. Moelans, A quantitative and thermodynamically consistent phase-field interpolation function for multi-phase systems, *Acta Materialia* 59 (3) (2011) 1077–1086.
- [54] S. M. Allen, J. W. Cahn, A microscopic theory for antiphase boundary motion and its application to antiphase domain coarsening, *Acta metallurgica* 27 (6) (1979) 1085–1095.
- [55] J. Ågren, Calculation of phase diagrams: Calphad, *Current opinion in solid state and materials science* 1 (3) (1996) 355–360.
- [56] S. D. Fabre, D. Guy-Bouyssou, P. Bouillon, F. Le Cras, C. Delacourt, Charge/discharge simulation of an all-solid-state thin-film battery using a one-dimensional model, *Journal of The Electrochemical Society* 159 (2) (2011) A104.
- [57] H.-K. Tian, Y. Qi, Simulation of the effect of contact area loss in all-solid-state li-ion batteries, *Journal of The Electrochemical Society* 164 (11) (2017) E3512.
- [58] C. P. Schmidt, S. Sinzig, V. Gravemeier, W. A. Wall, A three-dimensional finite element formulation coupling electrochemistry and solid mechanics on resolved microstructures of all-solid-state lithium-ion batteries, *Computer Methods in Applied Mechanics and Engineering* 417 (2023) 116468.
- [59] D. A. Cogswell, Quantitative phase-field modeling of dendritic electrodeposition, *Phys. Rev. E* 92 (2015) 011301. doi:10.1103/PhysRevE.92.011301.  
URL <https://link.aps.org/doi/10.1103/PhysRevE.92.011301>
- [60] Z. Hong, V. Viswanathan, Phase-field simulations of lithium dendrite growth with open-source software, *ACS Energy Letters* 3 (7) (2018) 1737–1743.
- [61] J. Jeon, G. H. Yoon, T. Vegge, J. H. Chang, Phase-field investigation of lithium electrodeposition at different applied overpotentials and operating temperatures, *ACS applied materials & interfaces* 14 (13) (2022) 15275–15286.
- [62] J. E. Guyer, W. J. Boettinger, J. A. Warren, G. B. McFadden, Phase field modeling of electrochemistry. ii. kinetics, *Physical Review E* 69 (2) (2004) 021604.

- [63] M. S. Whittingham, R. A. Huggins, Transport properties of silver beta alumina, *Journal of the Electrochemical Society* 118 (1) (1971) 1.
- [64] R. Fang, Y. Li, N. Wu, B. Xu, Y. Liu, A. Manthiram, J. B. Goodenough, Ultra-thin single-particle-layer sodium beta-alumina-based composite polymer electrolyte membrane for sodium-metal batteries, *Advanced Functional Materials* 33 (6) (2023) 2211229.
- [65] M. A. Muntaha, S. Chatterjee, S. Blondel, L. Aagesen, D. Andersson, B. Wirth, M. Tonks, Impact of grain boundary and surface diffusion on predicted fission gas bubble behavior and release in  $\text{UO}_2$  fuel (2023). [arXiv:2310.06795](https://arxiv.org/abs/2310.06795).
- [66] J. Zhang, A. F. Chadwick, P. W. Voorhees, Quantitative phase field model for electrochemical systems, *Journal of The Electrochemical Society* 170 (12) (2023) 120503.
- [67] H.-C. Yu, H.-Y. Chen, K. Thornton, Extended smoothed boundary method for solving partial differential equations with general boundary conditions on complex boundaries, *Modelling and Simulation in Materials Science and Engineering* 20 (7) (2012) 075008.
- [68] S. DeWitt, N. Hahn, K. Zavadil, K. Thornton, Computational examination of orientation-dependent morphological evolution during the electrodeposition and electrodisolution of magnesium, *Journal of The Electrochemical Society* 163 (3) (2015) A513.
- [69] G. Giudicelli, A. Lindsay, L. Harbour, C. Icenhour, M. Li, J. E. Hansel, P. German, P. Behne, O. Marin, R. H. Stogner, J. M. Miller, D. Schwen, Y. Wang, L. Munday, S. Schunert, B. W. Spencer, D. Yushu, A. Recuero, Z. M. Prince, M. Nezdyur, T. Hu, Y. Miao, Y. S. Jung, C. Matthews, A. Novak, B. Langley, T. Truster, N. Nobre, B. Alger, D. Andrš, F. Kong, R. Carlsen, A. E. Slaughter, J. W. Peterson, D. Gaston, C. Permann, 3.0 - MOOSE: Enabling massively parallel multiphysics simulations, *SoftwareX* 26 (2024) 101690. doi:<https://doi.org/10.1016/j.softx.2024.101690>.  
URL <https://www.sciencedirect.com/science/article/pii/S235271102400061X>
- [70] M. R. Tonks, D. Gaston, P. C. Millett, D. Andrs, P. Talbot, An object-oriented finite element framework for multiphysics phase field simulations, *Computational Materials Science* 51 (1) (2012) 20–29.
- [71] D. Schwen, L. K. Aagesen, J. W. Peterson, M. R. Tonks, Rapid multiphase-field model

- development using a modular free energy based approach with automatic differentiation in moose/marmot, *Computational Materials Science* 132 (2017) 36–45.
- [72] S. Hu, J. Murray, H. Weiland, Z. Liu, L. Chen, Thermodynamic description and growth kinetics of stoichiometric precipitates in the phase-field approach, *Calphad* 31 (2) (2007) 303–312.
- [73] M. Kellner, S. N. Enugala, B. Nestler, Modeling of stoichiometric phases in off-eutectic compositions of directional solidifying nbsi-10ti for phase-field simulations, *Computational Materials Science* 203 (2022) 111046.
- [74] M. V. Heinz, M.-C. Bay, U. F. Vogt, C. Battaglia, Grain size effects on activation energy and conductivity: Na- $\beta''$ -alumina ceramics and ion conductors with highly resistive grain boundary phases, *Acta Materialia* 213 (2021) 116940.
- [75] C. Wang, C. Sun, Z. Sun, B. Wang, T. Song, Y. Zhao, J. Li, H. Jin, Optimizing the na metal/solid electrolyte interface through a grain boundary design, *Journal of Materials Chemistry A* 10 (10) (2022) 5280–5286.
- [76] V. Yurkiv, J. S. Gutiérrez-Kolar, R. R. Unocic, A. Ramsubramanian, R. Shahbazian-Yassar, F. Mashayek, Competitive ion diffusion within grain boundary and grain interiors in polycrystalline electrodes with the inclusion of stress field, *Journal of the Electrochemical Society* 164 (12) (2017) A2830.
- [77] A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, et al., Commentary: The materials project: A materials genome approach to accelerating materials innovation, *APL materials* 1 (1) (2013).
- [78] G. A. Sullivan, J. W. Weymouth, Measurement of the equilibrium net vacancy concentration in sodium, *Physical Review* 136 (4A) (1964) A1141.
- [79] J. N. Mundy, Effect of pressure on the isotope effect in sodium self-diffusion, *Physical Review B* 3 (8) (1971) 2431.
- [80] A. R. West, *Solid state chemistry and its applications*, John Wiley & Sons, 2022.
- [81] S. Sinzig, C. P. Schmidt, W. A. Wall, A conservative and efficient model for grain boundaries of solid electrolytes in a continuum model for solid-state batteries, *Journal of The Electrochemical Society* 171 (4) (2024) 040505.

## Supporting Information

A diffuse-interface model for predicting the evolution of metallic negative electrodes and interfacial voids in solid-state batteries with homogeneous and polycrystalline solid electrolyte separators.

Sourav Chatterjee<sup>a,b</sup>, Michael Tonks<sup>a</sup>, William Gardner<sup>c</sup>, Marina Sessim<sup>c</sup>

<sup>a</sup>Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611, USA,

<sup>b</sup>Materials Science Division, Lawrence Livermore National Laboratory, Livermore, CA 94550, USA,

<sup>c</sup>QuantumScape Battery, Inc., 1730 Technology Drive, San Jose, CA 95110, USA

### *S.1. Derivation of the grand-potential expressions*

As discussed in Section 3, we assume that the free energy densities of the auxiliary phase, metallic negative electrode, and void are parabolic functions of the Na mole fractions. This yields:

$$f_p(c_{Na}^p) = \frac{A^p}{2}(c_{Na}^p - c_{Na}^{eq,p})^2 \quad p = a, m, v \quad \text{in} \quad \Omega_{ed}. \quad (\text{S.1})$$

The diffusion potential of Na in the region  $\Omega^{ed}$  is then obtained from Eq. (S.1) using  $\mu_{Na}^{ed} = v_m(df_p/dc_{Na}^p)$ , which yields:  $\mu_{Na}^{ed}(c_{Na}^p) = v_m A^p(c_{Na}^p - c_{Na}^{eq,p})$ . This relation can be inverted to obtain the phase mole fractions as functions of Na diffusion potential, which is the independent variable in our model:

$$c_{Na}^p(\mu_{Na}^{ed}) = \frac{\mu_{Na}^{ed}}{A^p v_m} + c_{Na}^{eq,p} \quad p = a, m, v \quad \text{in} \quad \Omega_{ed}. \quad (\text{S.2})$$

Substituting Eq. (S.2) in Eq. (3) yields the grand-potential densities of the auxiliary phase, metallic negative electrode, and void as functions of Na diffusion potential:

$$\omega_p(\mu_{Na}^{ed}) = - \left[ \frac{(\mu_{Na}^{ed})^2}{v_m^2 A^p} + \frac{\mu_{Na}^{ed} c_{Na}^{eq,p}}{v_m} \right] \quad p = a, m, v \quad \text{in} \quad \Omega_{ed}. \quad (\text{S.3})$$

### *S.2. Stripping and plating rates based on a sharp-interface electrochemical model*

In a sharp-interface electrochemical model, the velocity of the electrode/electrolyte interface,  $v_{ed/el}$ , is given by Faraday's law [1]:

$$v_{ed/el} = -\frac{M_w}{\rho} \frac{i_{ed/el}}{F}, \quad (\text{S.4})$$

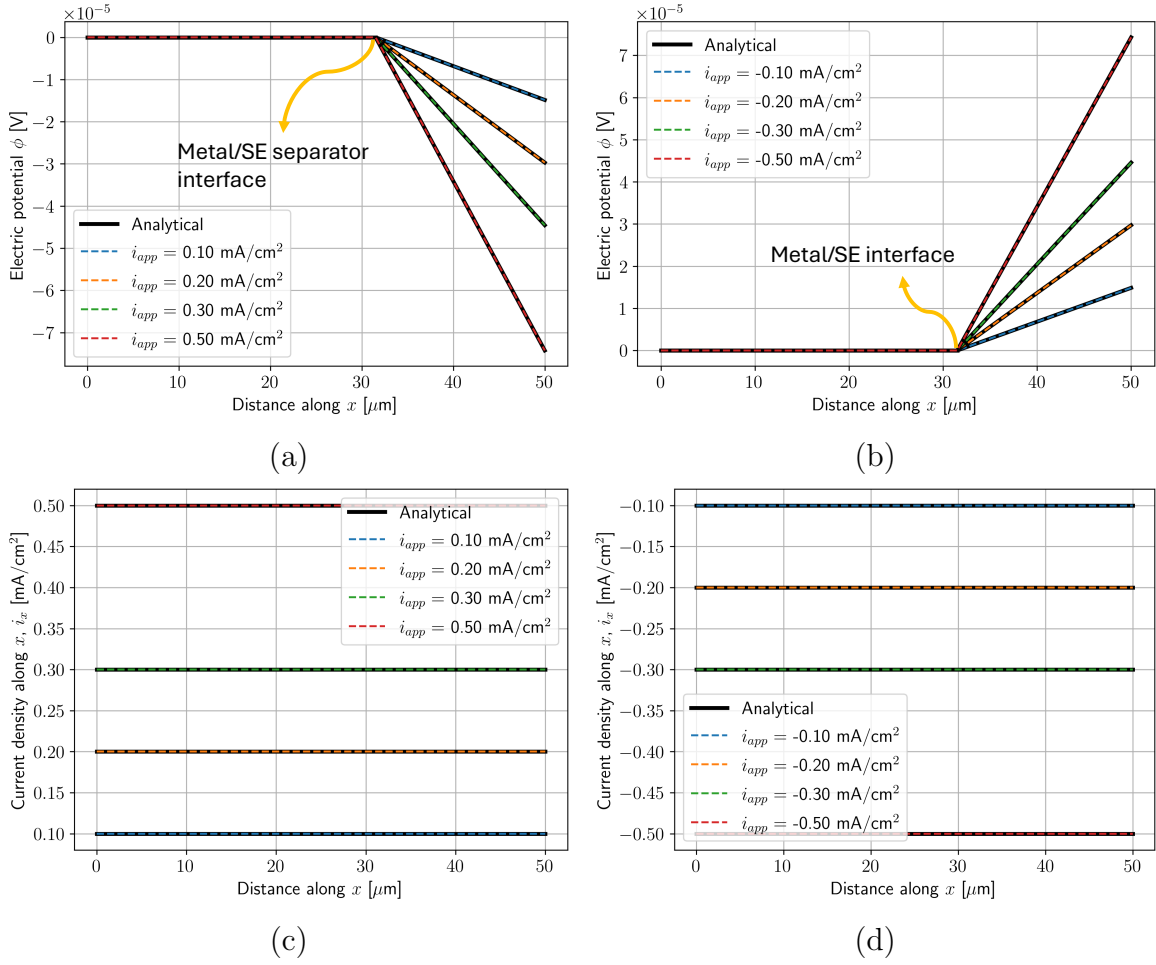
where  $M_w$  is the molar mass of the metal,  $\rho$  is the density of the metal,  $F$  is Faraday constant, and  $i_{ed/el}$  is the interfacial current at the electrode/electrolyte interface. It should be noted that the deposition/depletion rates depend on the velocity of the electrode/electrolyte interface in a sharp-interface model. Thus, we refer to Eq. (S.4) as the sharp-interface deposition/depletion rates.

We make two assumptions to compare our simulated deposition/depletion rates with the sharp-interface rates. First, we assume the molar mass  $M_w$  and density  $\rho$  of the Na negative electrode to be 22.98 g/mol and 0.9688 g/cm<sup>3</sup> [2], respectively. Second, we assume that the interfacial current density in Eq. (S.4) equals the applied current density in our simulation, i.e.,  $i_{ed/el} = i_{app}$ . This is reasonable because the electrode/electrolyte interface is perfect and planar, which leads to a homogeneous current density distribution, as shown in Fig. S3.

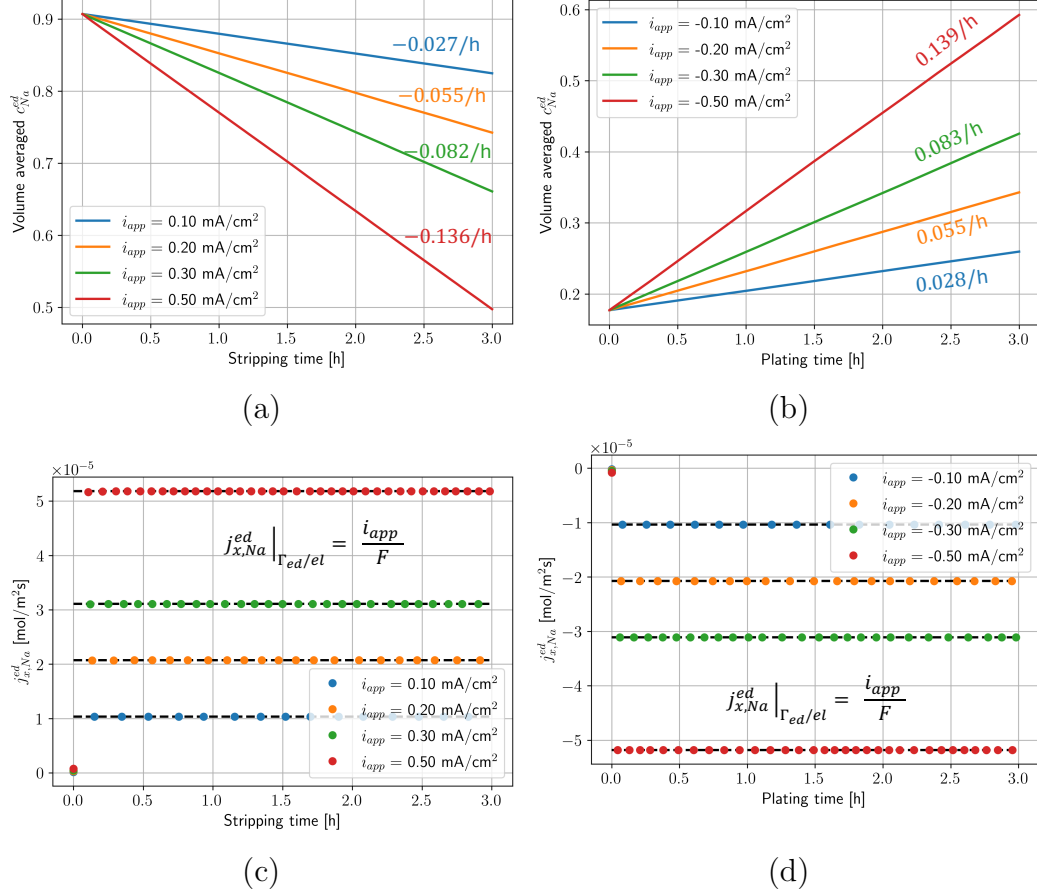
### *S.3. Verification of charge and mass conservation equations and interfacial flux evolution in cases with perfect electrode/electrolyte interface.*

To verify that the charge is conserved in our model, we compare the simulated electric potential and current density in cases with a perfect electrode/electrolyte interface (Section 4.1.1) with an analytical solution (see Section S.4 of the Supporting Information for details). Figures S1a and S1b show that the electric potential is almost negligible along the  $x$  axis within the auxiliary and Na electrode phases, while it varies linearly across the homogeneous SE separator during stripping and plating for any given applied current density. Note that these results are independent of time. Furthermore, the slope of the electric potential in the solid electrolyte separator varies with the applied current density and is consistent with the analytical solution. Consequently, the current density is constant along the  $x$  axis and equal to the applied current density during stripping and plating (Figs. S1c and S1d). Since the domain and boundary conditions are homogeneous in the  $y$  direction, the electric potential is constant in the  $y$  direction and the current density in the  $y$  direction is zero (Fig. S3). These results verify that the charge is conserved in our model.





**Fig. S1.** Verification of charge conservation equation in cases with perfect electrode/electrolyte interface. The spatial distribution of electric potential during (a) stripping and (b) plating. Spatial distribution of current density along the x axis during (c) stripping and (d) plating.



**Fig. S2.** Variation in volume-averaged Na mole fraction  $c_{Na}$  with time during (a) stripping and (b) plating. Values of the slopes obtained by linear fitting of the curves are shown in (a) and (b). The temporal variation in the  $x$  component of the area-averaged mass flux of Na at the electrode/electrolyte interface, denoted as  $j_{x,Na}^{ed}$ , during (c) stripping and (d) plating. The dotted lines in (c) and (d) indicate the ratio of applied current density to the Faraday constant.

Next, we verify that mass is conserved in our model. It should be noted that due to the shrinkage and growth of the Na electrode, the overall Na concentration in the electrode-auxiliary ( $\Omega_{ed}$ ) region decreases and increases during stripping and plating, respectively. To verify this, we calculated the volume-averaged mole fraction of Na using Eq. (S.17) provided in Section S.5 of the Supporting Information. Figures S2a and S2b show that the overall Na concentration decreases and increases linearly with time during stripping and plating for different applied current densities. Note that the growth of the auxiliary phase does not contribute significantly to the overall Na concentration because the mole fraction of Na in the auxiliary phase is negligible ( $\approx 10^{-6}$ ), as shown in Fig. S3. The concentration in the auxiliary phase deviates slightly from the equilibrium value ( $10^{-8}$ ) because the diffusion potential within the auxiliary phase is not exactly zero. This shift in the diffusion potential from zero is due to the flux boundary condition at the electrode/electrolyte interface (Eq. (16)) which induces a gradient in the diffusion potential within the electrode. The slopes, i.e., the Na loss and gain rates, obtained after linear fitting are also shown in Figs. S2a and S2b, and are proportional to the applied current density. We also analytically calculate the Na loss and gain rates (see Section S.5 of the Supporting Information). Table S.1 shows that the calculated Na loss rates agree with the analytical values. Note that the difference between the Na loss and gain rates is negligible ( $\leq 1\%$ ). This verifies that the mass is conserved in our simulations. It is important to note that mass conservation in moving sharp-interface electrochemical models is often an issue, especially during cycling simulations, and can require a reformulation of the interfacial conditions at the moving electrode/electrolyte interface [1, 3]. Our approach naturally conserves mass and does not require interfacial conditions at the moving interface.

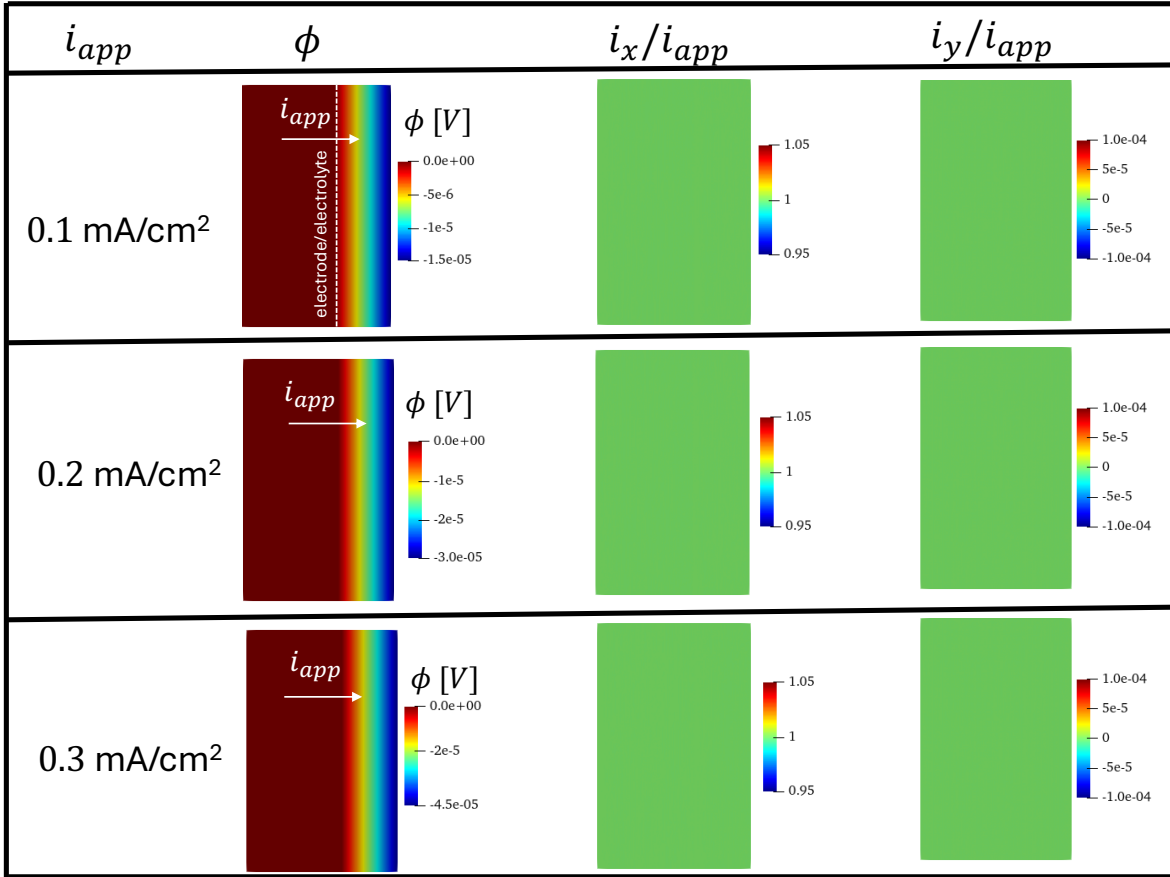
Finally, we also verify that the flux at the electrode/electrolyte interface is constant with time in the perfect interface cases. Thus, we calculate the area-averaged flux of Na in the  $x$  direction at the electrode/electrolyte interface using Eq. (S.21) (see Section S.10 of the Supporting Information). Figures S2c and S2d depict the area-averaged flux of Na in the  $x$  direction at the electrode/electrolyte interface as a function of time during stripping and plating for different applied current densities. As expected, the average interfacial flux remains constant over time and is equal to the ratio of the applied current density to the Faraday constant, specifically  $i_{app}/F$ . The ratio is indicated by dotted black lines in Figs. S2c and S2d.

**Table S.1**

Na loss and gain rates during stripping and plating calculated using an analytical approach and our predicted values. The analytical approach is described in Section S.5 of the Supporting Information. The predicted loss and gain rates were obtained by linearly fitting the simulated curves shown in Figs. S2a and S2b, respectively.

| $i_{app}$ [mA/cm <sup>2</sup> ]                    | $\pm 0.1$   | $\pm 0.2$   | $\pm 0.3$   | $\pm 0.5$   |
|----------------------------------------------------|-------------|-------------|-------------|-------------|
| Analytical [h <sup>-1</sup> ]                      | $\mp 0.028$ | $\mp 0.056$ | $\mp 0.084$ | $\mp 0.141$ |
| Stripping <sup>This paper</sup> [h <sup>-1</sup> ] | -0.027      | -0.055      | -0.082      | -0.136      |
| Plating <sup>This paper</sup> [h <sup>-1</sup> ]   | +0.028      | +0.055      | +0.083      | +0.139      |

#### S.4. Analytical solution for the charge conservation equation



**Fig. S3.** Results of the stripping simulation with a perfect electrode/electrolyte interface and a homogeneous SE separator after 3 h. The first column shows the applied stripping current densities,  $i_{app}$  in units of mA/cm<sup>2</sup>; the second column shows the spatial distribution of electric potential  $\phi$  across the domain in units of volts; the third column shows the spatial distribution of current density along the x-axis normalized by the applied current density,  $i_x/i_{app}$ ; the fourth column shows the spatial distribution of current density along the y-axis normalized by the applied current density,  $i_y/i_{app}$ .

In this section, an analytical solution for the charge conservation equation is derived assuming a perfect electrode/electrolyte interface and a homogeneous solid electrolyte separator. Figure S3 shows

that the spatial distributions of electric potential and current density along the  $y$  axis are uniform in cases with a perfect electrode/electrolyte interface. Thus, the electrostatic problem can be reduced to a one-dimensional problem. Since the electronic conductivity of the auxiliary phase equals the metallic negative electrode, the electric current in the region  $\Omega_{ed}$  may be written as  $i^{ed} = -\sigma_m (d\phi^{ed}/dx)$ . Consequently, Eq. (10) yields:

$$\sigma_m \frac{\partial^2 \phi^{ed}}{\partial x^2} = 0 \quad \text{in} \quad \Omega^{ed}. \quad (\text{S.5})$$

Likewise, since the solid electrolyte separator is homogeneous, the ionic current in the region  $\Omega_{ed}$  may be written as  $i^{el} = -\kappa_g^{el} (d\phi^{el}/dx)$ . Consequently, Eq. (11) yields:

$$\kappa_g^{el} \frac{\partial^2 \phi^{el}}{\partial x^2} = 0 \quad \text{in} \quad \Omega^{el}. \quad (\text{S.6})$$

The general form of electric potentials that satisfy Eqs. (S.5) and (S.6) are:

$$\phi^{ed}(x) = \mathcal{A}^{ed}x + \mathcal{B}^{ed}, \quad (\text{S.7})$$

$$\phi^{el}(x) = \mathcal{A}^{el}x + \mathcal{B}^{el}, \quad (\text{S.8})$$

where  $\mathcal{A}^{ed}$ ,  $\mathcal{B}^{ed}$ ,  $\mathcal{A}^{el}$ , and  $\mathcal{B}^{el}$  are four unknown constants. These four unknowns can be determined from the four boundary conditions. Two of these boundary conditions follow from the interfacial conditions, i.e., Eqs. (14) and (15). Thus, using Eqs. (S.7) and (S.8) in Eqs. (14) and (15), we obtain

$$\phi^{ed}|_{x=x_{in}} = \phi^{el}|_{x=x_{in}} \implies \mathcal{A}^{ed}x_{in} + \mathcal{B}^{ed} = \mathcal{A}^{el}x_{in} + \mathcal{B}^{el}, \quad (\text{S.9})$$

$$i^{ed}|_{x=x_{in}} = i^{el}|_{x=x_{in}} \implies \sigma_m \mathcal{A}^{ed} = \kappa_g^{el} \mathcal{A}^{el}, \quad (\text{S.10})$$

where  $x_{in}$  is the position of the electrode/electrolyte interface. Note that the electrode/electrolyte interface does not vary with time in our simulations. The remaining two boundary conditions are at the left and right boundaries. At the left boundary, i.e.,  $x = 0$ , Eq. (17) yields:

$$\phi^{ed}|_{x=0} = 0 \implies \mathcal{B}^{ed} = 0. \quad (\text{S.11})$$

Similarly, at the right boundary, i.e.,  $x = L$ , where  $L$  is the length of the domain, Eq. (18) yields

$$i^{el}|_{x=L} = i_{app} \implies \mathcal{A}^{el} = \frac{i_{app}}{\kappa_g^{el}}. \quad (\text{S.12})$$

The remaining two unknowns are obtained by substituting Eqs. (S.11) and (S.12) into Eqs. (S.9) and (S.10), which gives:

$$\mathcal{B}^{el} = \left[ \frac{\kappa_g^{el}}{\sigma_m} - 1 \right] i_{app} x_{in} \quad (\text{S.13})$$

$$\mathcal{A}^{ed} = \frac{\kappa_g^{el}}{\sigma_m} \mathcal{A}^{el} = \frac{\kappa_g^{el}}{\sigma_m} \frac{i_{app}}{\kappa_g^{el}} \quad (\text{S.14})$$

### S.5. Analytical solution for Na loss and gain rates

In this section, we calculate the Na loss or gain rates during stripping or plating analytically using the mass conservation equation, i.e., Eq. (7):

$$\frac{1}{v_m} \frac{\partial c_{Na}^{ed}}{\partial t} + \nabla \cdot \mathbf{j}_{Na}^{ed} = 0, \quad \text{in } \Omega_{ed}. \quad (\text{S.15})$$

Since the flux of Na is non-zero only at the electrode/electrolyte interface, taking the volume-integral of this equation and using the divergence theorem, Eq. (S.15) may be written as:

$$\int_{\Omega_{ed}} \frac{1}{v_m} \frac{\partial c_{Na}^{ed}}{\partial t} dv = - \int_{A_{ed}} \mathbf{j}_{Na}^{ed/el} \cdot \mathbf{n}_{ed/el} da, \quad (\text{S.16})$$

where  $\int_{A_{ed}}$  indicates the surface integral of the flux over the electrode/electrolyte interface,  $\mathbf{j}_{Na}^{ed/el}$  is the flux at the electrode/electrolyte interface, and  $\mathbf{n}_{ed/el}$  is the unit normal at the electrode/electrolyte interface (Fig. 1a). Further, the volume-averaged Na mole fraction,  $\langle c_{Na} \rangle$ , is defined as:

$$\langle c_{Na} \rangle = \frac{\int_{\Omega_{ed}} c_{Na}^{ed} dv}{V_{ed}}, \quad (\text{S.17})$$

where  $V_{ed}$  is the volume of the subregion  $\Omega_{ed}$ . Dividing Eq. (S.16) by  $V_{ed}$  and using Eq. (S.17) yields:

$$\frac{\partial \langle c_{Na} \rangle}{\partial t} = - \frac{v_m}{V_{ed}} \int_{A_{ed}} \mathbf{j}_{Na}^{ed/el} \cdot \mathbf{n}_{ed/el} da. \quad (\text{S.18})$$

By integrating Eq. (16) over the area of the electrode/electrolyte interface and assuming that the normal component of the solid electrolyte current density is uniform along the electrode/electrolyte interface, the integral term in Eq. (S.18) can be expressed as

$$\int_{A_{ed}} \mathbf{j}_{Na}^{ed/el} \cdot \mathbf{n}_{ed/el} da = \frac{i_x^{el}|_{\Gamma_{ed/el}} A_{ed}}{F}, \quad (\text{S.19})$$

where  $A_{ed}$  is the area of the perfect electrode/electrolyte interface. In cases with a perfect electrode/electrolyte interface, the normal current density at the electrode/electrolyte interface ( $i_x^{el}|_{\Gamma_{ed/el}}$ ) is uniform and equal to the applied current density  $i_{app}$  (Fig. S3). Thus, substituting Eq. (S.19) in Eq. (S.18) and using  $A_{ed}/V_{ed} = L_{ed}$ , where  $L_{ed}$  is the thickness of the region  $\Omega_{ed}$ , yields:

$$\frac{\partial \langle c_{Na} \rangle}{\partial t} = -\frac{v_m}{L_{ed}} \frac{i_{app}}{F}, \quad (\text{S.20})$$

where  $\partial \langle c_{Na} \rangle / \partial t$  denotes the analytically obtained Na loss or gain rate.

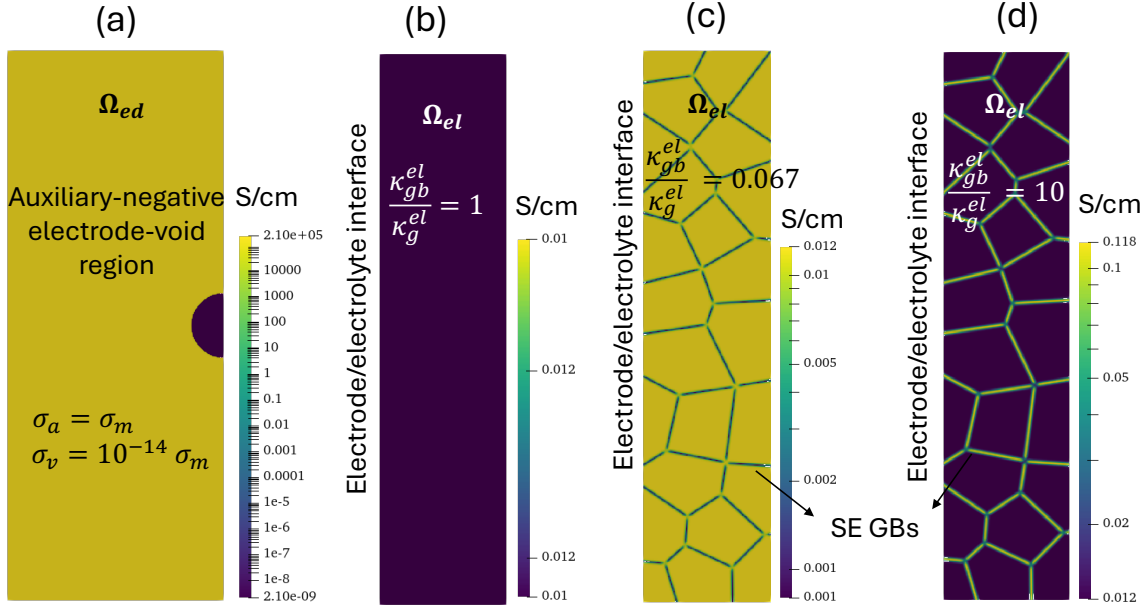
#### S.6. Spatial variation in conductivity in cases with a single void at the electrode/electrolyte interface

In the simulations with polycrystalline SE, the grain structure is created using a Voronoi tessellation. The value of the ionic conductivity varies along the grain boundaries, as shown in Fig. S4.

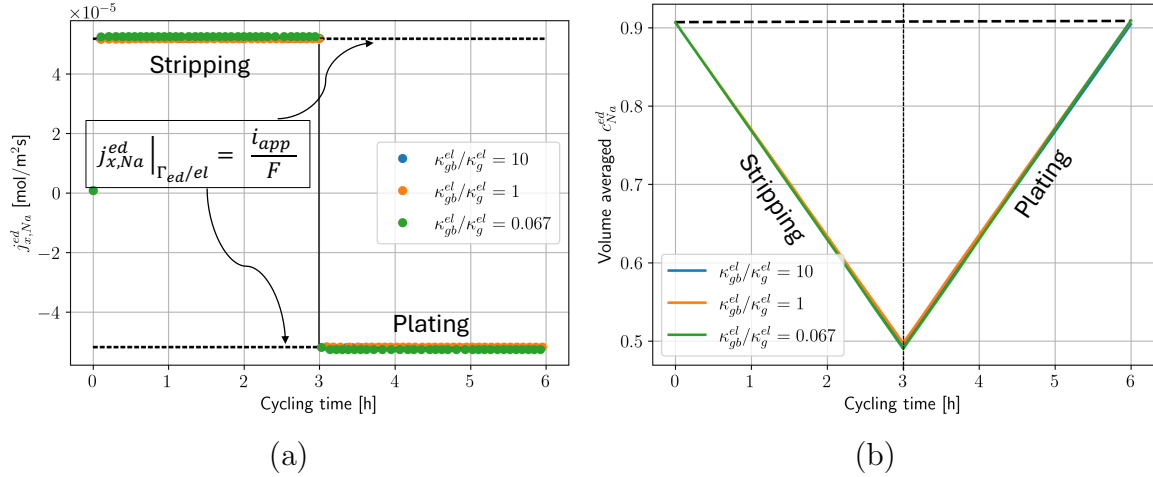
#### S.7. Interfacial flux and mass conservation during cycling of a Na electrode in perfect contact with a polycrystalline solid electrolyte

Figure S5a shows the temporal variation in the average flux of Na at the electrode/electrolyte interface for different GB-to-grain conductivity ratios. As expected, the steady-state fluxes are independent of the GB-to-grain conductivity ratios and are equal to the ratio of applied cycling current density divided by the Faraday constant,  $i_{app}/F$ . This explains the absence of significant variations in the deposition and depletion rates during cycling with different GB-to-grain conductivity ratios, as shown in Fig. 6a. It also confirms our assertion that the deposition and depletion rates mainly depend on the magnitude of the applied current density.

Figure S5b shows the total Na concentration during cycling for different GB-to-grain conductivity ratios. The overall Na loss and gain rates during cycling are independent of the GB-to-grain conductivity ratios. This is also consistent with our analysis in Section 4.1.1, which shows that the Na loss or gain rates depend only on the applied flux at the electrode/electrolyte interface. Since this flux is



**Fig. S4.** Simulation domain for the simulations with polycrystal SE separators. (a) Spatial distribution of electronic conductivity in the region  $\Omega_{ed}$ . Spatial distribution of ionic conductivity in the region  $\Omega_{el}$  for (b) homogeneous SE ( $\kappa_{gb}^{el}/\kappa_g^{el} = 1$ ), (c) low-conductivity SE ( $\kappa_{gb}^{el}/\kappa_g^{el} = 0.067$ ), and (d) high-conductivity SE ( $\kappa_{gb}^{el}/\kappa_g^{el} = 10$ ).

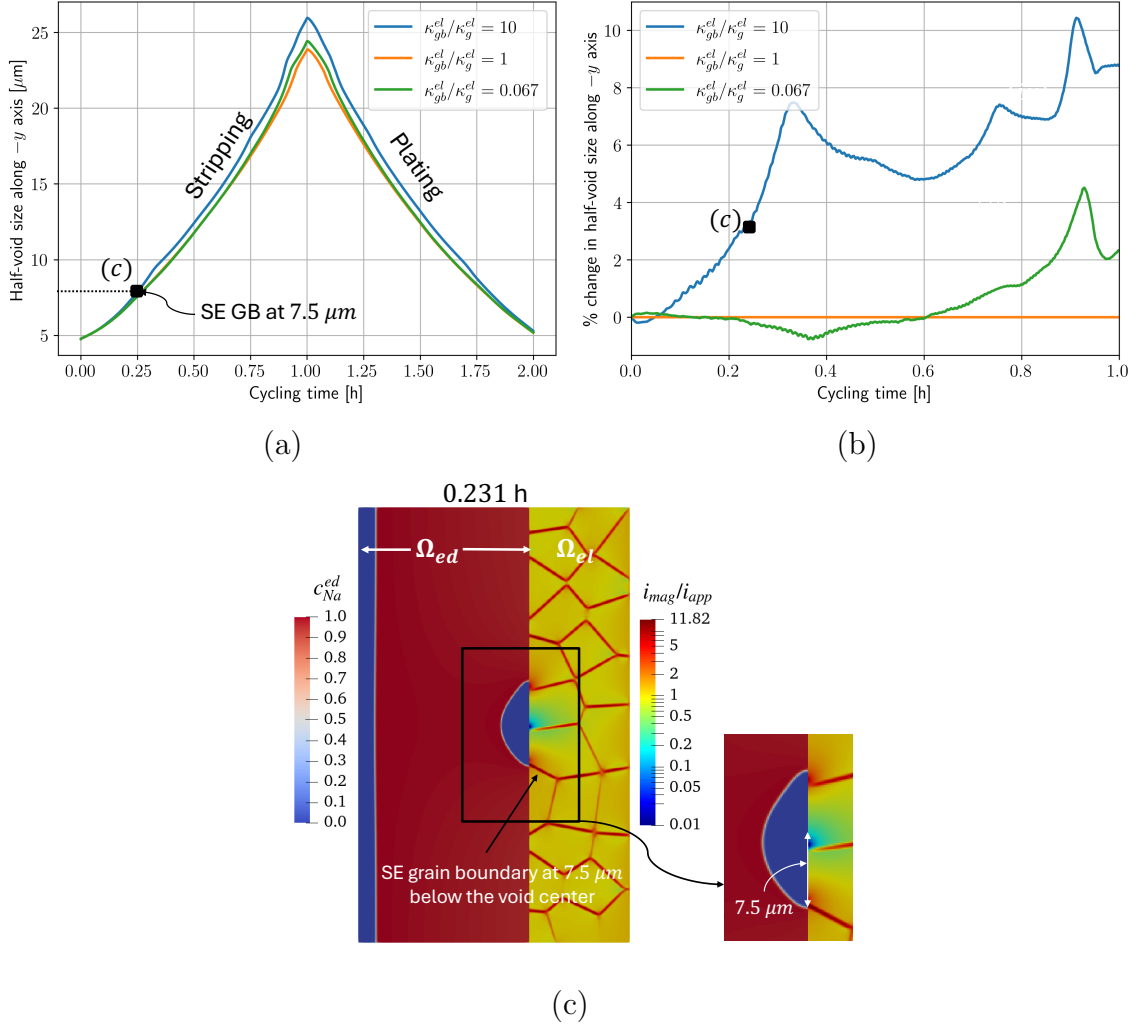


**Fig. S5.** (a) The temporal variation in the  $x$  component of the area-averaged mass flux of Na at the electrode/electrolyte interface, denoted as  $j_{x,Na}^{ed}$ , during cycling with SEs having low-conductivity ( $\kappa_{gb}^{el}/\kappa_g^{el} = 0.067$ ), homogeneous ( $\kappa_{gb}^{el}/\kappa_g^{el} = 1$ ) and high-conductivity ( $\kappa_{gb}^{el}/\kappa_g^{el} = 10$ ) GBs. The dotted lines in (a) indicate the ratio of applied current density to the Faraday constant. (b) Volume-averaged Na mole fraction over time for different GB-to-grain conductivity ratios. In (b), the black dotted line indicates the initial and final concentrations of Na in the system.



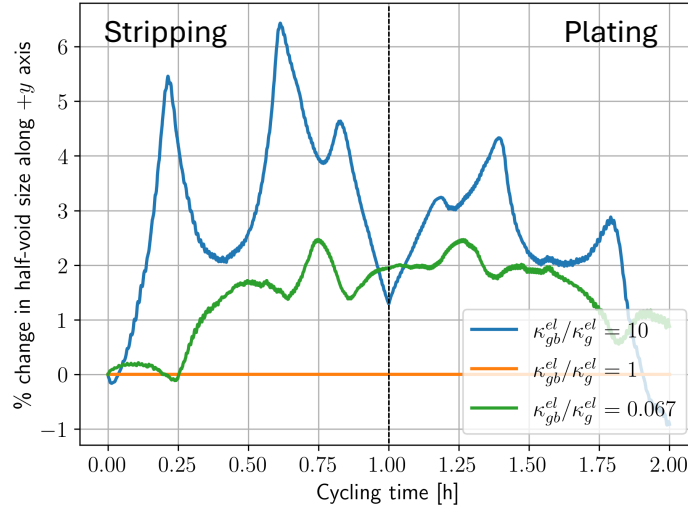
identical in the case of polycrystalline and homogenous SEs, as shown in Fig. S5a, the Na loss and gain rates during cycling are identical. The initial and final total Na concentrations are equal, indicating that the mass of Na is conserved in our cyclic simulations regardless of the SE GB properties.

#### S.8. Void/GB interaction along the negative y axis



**Fig. S6.** Analysis of cycling simulations with a single interfacial void at the interface between the negative electrode and a polycrystalline SE separator. (a) Half-void size below the void center with cycling time for SEs with low-conductivity ( $\kappa_{gb}^{el}/\kappa_g^{el} = 0.067$ ), homogeneous ( $\kappa_{gb}^{el}/\kappa_g^{el} = 1.0$ ), and high-conductivity ( $\kappa_{gb}^{el}/\kappa_g^{el} = 10$ ) GBs. (b) Percentage change in lower half-void size relative to the homogeneous SE as a function of stripping time for  $\kappa_{gb}^{el}/\kappa_g^{el} = 0.067$ , 1 and 10. Simulation domain at the instant when the lower void edge touches a high-conductivity SE GB at a distance of  $7.5 \mu\text{m}$  below the void centre. In (c),  $\Omega_{ed}$  is shaded by the Na concentration and  $\Omega_{el}$  by the normalized current density. In (a) and (b), the black marker labelled (c) corresponds to the microstructure shown in Fig. S6c.

S.9. Complete plot of the percentage change in half-void size along the +y-axis with cycling time



**Fig. S7.** Percentage change in upper half-void size relative to the homogeneous solid electrolyte (SE) ( $\kappa_{gb}^{el}/\kappa_g^{el} = 1$ ) as a function of cycling time for low-conductivity ( $\kappa_{gb}^{el}/\kappa_g^{el} = 0.067$ ) and high-conductivity ( $\kappa_{gb}^{el}/\kappa_g^{el} = 10$ ) grain boundaries (GBs).

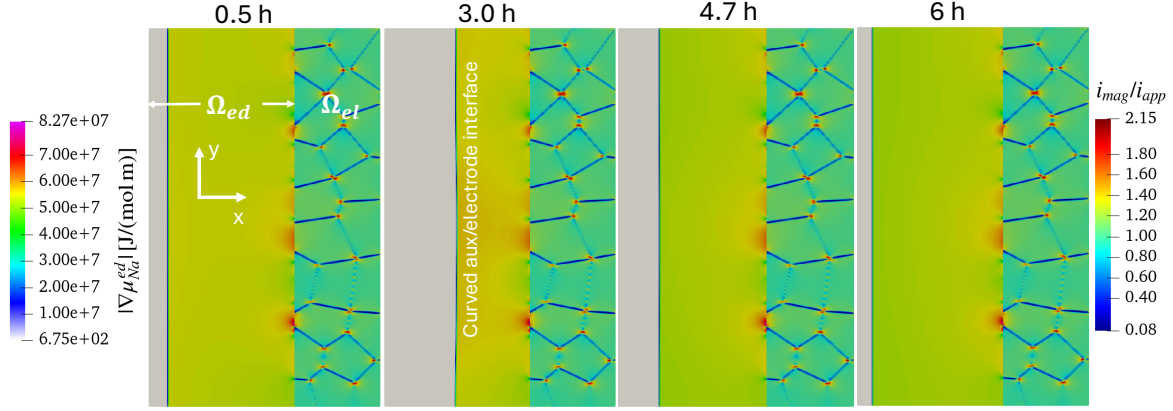
S.10. Definition of area-averaged flux of Na

The area-averaged flux of Na in the  $x$  direction at time  $t$  is defined as follows:

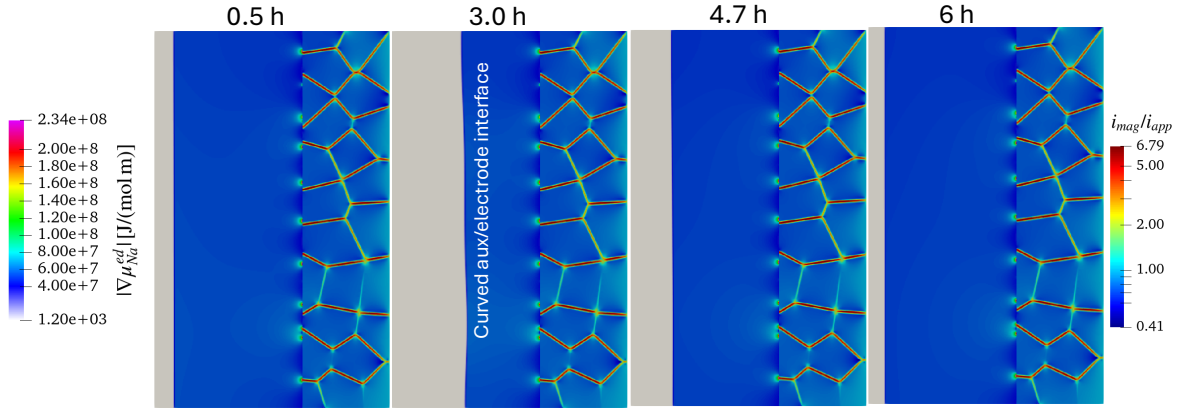
$$j_{x,Na}^{ed}(t) = \frac{1}{A_{ed}} \int_{A_{ed}} j_{x,Na}^{ed}(\mathbf{x}, t) \big|_{\Gamma_{ed/el}} da, \quad (\text{S.21})$$

where  $A_{ed}$  is the area of the perfect electrode/electrolyte interface and  $j_{x,Na}^{ed} \big|_{\Gamma_{ed/el}}$  is the flux of Na at the electrode/electrolyte interface, which may vary with position  $\mathbf{x}$  and time  $t$ .

S.11. Spatial distribution of the gradient in the diffusion potential of sodium within the electrode



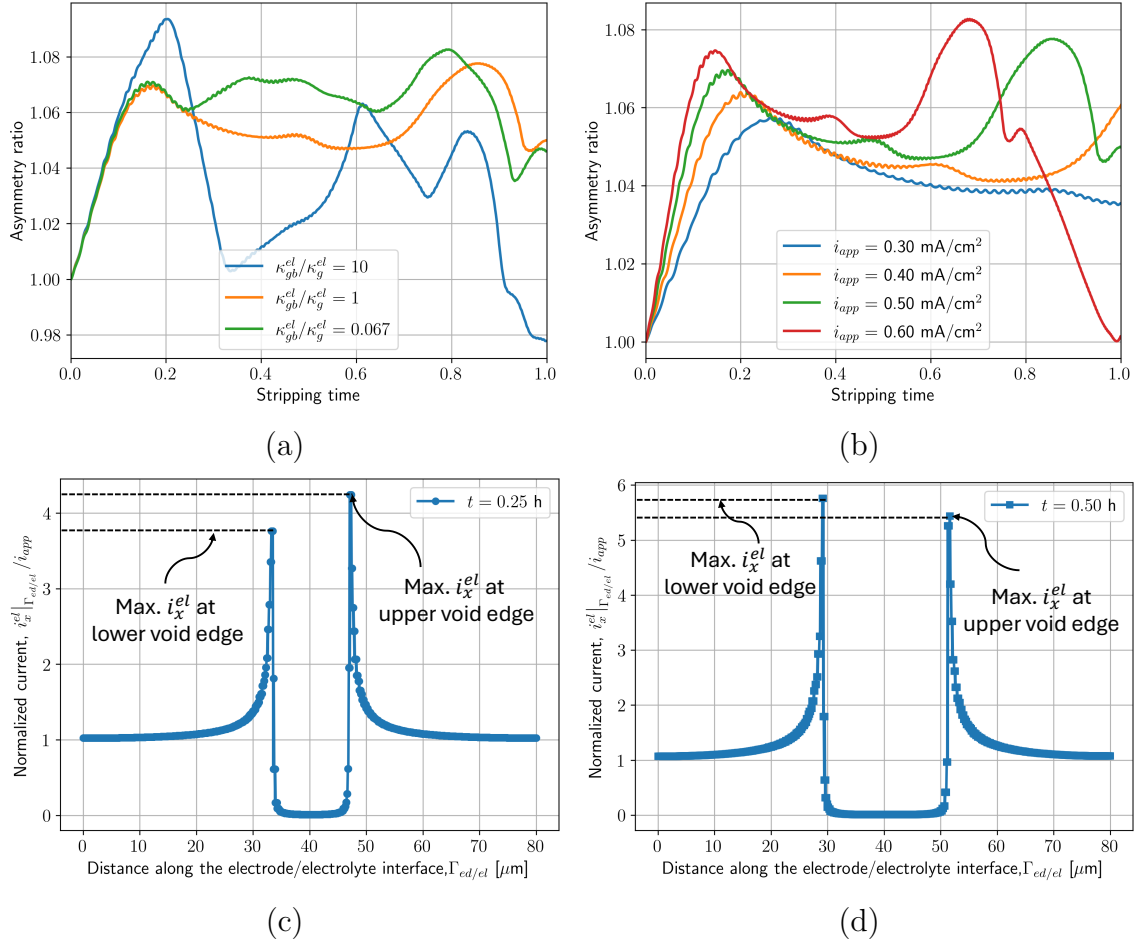
(a)



(b)

**Fig. S8.** Cycling simulations assuming a perfect electrode/electrolyte interface and polycrystalline SE separator. Evolution of the Na negative electrode during cycling under an applied current density of  $0.5 \text{ mA/cm}^2$  with (a)  $\kappa_{gb}^{el}/\kappa_g^{el} = 0.067$  and (b)  $\kappa_{gb}^{el}/\kappa_g^{el} = 10$ .  $\Omega_{ed}$  is shaded by the magnitude of the diffusion potential gradient ( $|\nabla\mu_{Na}^{ed}|$ ) and  $\Omega_{el}$  by the ratio of the local current density to the applied current density.

### S.12. Asymmetry in void growth during stripping



**Fig. S9.** The variation in the asymmetry ratio as a function of stripping time for different (a) GB-to-grain conductivity ratios and (b) applied current densities. The asymmetry ratio is defined as the ratio of the distances from the void center to the upper and lower void edges. Spatial distribution of the normal component of the electrolyte current density ( $i_x^{el}$ ) along the electrode/electrolyte interface,  $\Gamma_{ed/el}$ , at times (c) 0.25 h and (d) 0.50 h. The current density is normalized by the applied current density,  $i_{app}$ , which equals 0.5 mA/cm<sup>2</sup>. In (b) and (c), the block dotted lines indicate the maximum value of current near the void edges.

Figure S9a shows the temporal variation in the asymmetry ratio for cases with homogeneous ( $\kappa_{gb}^{el}/\kappa_g^{el} = 1$ ), low grain boundary conductivity ( $\kappa_{gb}^{el}/\kappa_g^{el} = 0.067$ ) and high grain boundary conductivity ( $\kappa_{gb}^{el}/\kappa_g^{el} = 10$ ) SE separators during stripping under an applied current density of 0.5 mA/cm<sup>2</sup>. The asymmetry ratio is determined as the ratio of the distance from the void center to the upper and lower void edges. This ratio marginally deviates from 1 in the homogeneous SE case, suggesting that void growth is not perfectly symmetric (Fig. S9a), which is counterintuitive. To account for this, note that the void growth rate depends on the magnitude of the flux of Na concentrated near the void

edges (Section 4.2.1). The magnitude of this flux, in turn, is proportional to the normal component of the electrolyte current density,  $i_x^{el}$ , as discussed in Section 2.3. Thus, if the distribution of the normal component of the electrolyte current density  $i_x^{el}$  is not perfectly symmetric about the void center and along the electrode/electrolyte interface, it can result in asymmetric void growth.

Figures S9c and S9d show the spatial distribution of the normal component of electrolyte current ( $i_x^{el}$ ) along the electrode/electrolyte interface after stripping for 0.25 h and 0.50 h, respectively, in the case of a homogeneous SE separator. In these figures, the current density is normalized by the applied current density ( $i_{app}$ ), which equals 0.5 mA/cm<sup>2</sup>. These figures reveal that the spatial distribution of the normal component of the current density along the electrode/electrolyte interface is slightly asymmetric during stripping. This is evident by the asymmetry in the maximum current densities at the lower and upper void edges, thus explaining the observed asymmetry in the void growth rate in the homogeneous SE case in Fig S9a. The figures also depict that the current is concentrated and exhibits significant gradients near the void edges. The current density distribution is slightly asymmetric because the electrolyte domain has been discretized using linear quadrilateral finite elements. Employing higher-order finite elements or a more refined mesh may improve the symmetry of the current distribution near the void edges by reducing the discretization error, though at higher computational costs. As demonstrated in Section 2.1, the electrolyte current density becomes more concentrated with increasing magnitude of the applied current density. This consequently causes increased gradients in current density near void edges and increases the asymmetry in the current density distribution. As a result, the asymmetry in void growth also increases with the magnitude of the applied current density, as illustrated in Fig. S9b. However, the maximum deviation relative to a perfectly symmetric growth is marginal ( $\leq 8\%$ ).

Figure S9a also shows that the asymmetry ratio, and thus void size, marginally varies with grain boundary (GB) conductivity, which is intuitive, because the magnitude of the normal component of the current density along the electrode/electrolyte interface depends on the GB conductivity. This explains why the deviation in the asymmetry ratio, as compared to the homogeneous SE case, is higher in the high-GB conductivity SE case than in the low-GB conductivity SE case (Fig. S9a).

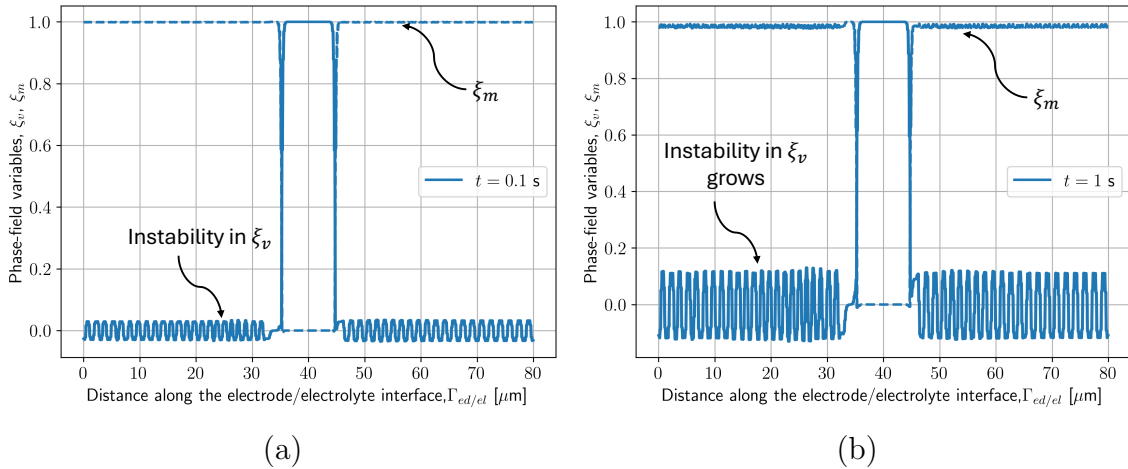
### *S.13. Instability in phase-field variables in case with arbitrarily high $A_p$*

In Section 3, we suggested that the value of  $A_p$  is selected “high” enough so that the Na concentrations within the void and electrode phases do not significantly deviate from the equilibrium values. However, this value cannot be arbitrarily high as it may lead to instability in the void phase-field

variable.

To show this, we performed a stripping simulation with an interfacial void in contact with a homogeneous SE separator under an applied current density of  $0.5 \text{ mA/cm}^2$  with  $A_p$  values  $10^3$  times higher than the values reported in Table 1. The initial and boundary conditions are identical to the cases discussed in Section 4.2.1.

Figures S10a and S10b show that the phase-field variable representing the void phase ( $\xi_v$ ) exhibits instability during stripping with high  $A_p$  values. To understand why this occurs near the electrode/electrolyte interface, note that a high  $A^p$  value would reduce the mobilities  $M_p$  for a given diffusivity value, as  $M_p = D_M^p dc_M^p / d\mu_M^{ed} = D_M^p / (A^p v_m)$ . Reduced mobilities can induce significantly large gradients in the diffusion potential of Na within the electrode. This, consequently, would increase the absolute value of the diffusion potential of Na along the electrode/electrode interface for the same magnitude of the applied current density. Consequently, the bulk driving force of the phase-field variable becomes very high, thus causing its instability. In a grand-potential-based phase-field model, the bulk driving force of the phase-field variable is defined as the difference in the bulk grand potential densities of the adjacent phases [4]. In our context, this can be specifically written as:  $\omega_m(\mu_{Na}^{ed}) - \omega_v(\mu_{Na}^{ed})$ . Note that this driving force depends on the diffusion potential of Na. Thus, if the absolute value of the diffusion potential increases, the bulk driving force of the phase-field variable also increases, thereby causing its instability. It is important to acknowledge that the instability of the phase-field variable due to high bulk driving forces has also been reported by other researchers [5, 6].



**Fig. S10.** Spatial distribution of the phase-field variables denoting the void phase ( $\xi_v$ ) and metal phase ( $\xi_m$ ) along the electrode/electrolyte interface after stripping for (a) 0.1 s and (b) 1 s.

## References

- [1] L. Mishra, A. Subramaniam, T. Jang, K. Shah, M. Uppaluri, S. A. Roberts, V. R. Subramanian, Perspective—mass conservation in models for electrodeposition/stripping in lithium metal batteries, *Journal of The Electrochemical Society* 168 (9) (2021) 092502.
- [2] S. Kim, J. Chen, T. Cheng, A. Gindulyte, J. He, S. He, Q. Li, B. A. Shoemaker, P. A. Thiessen, B. Yu, et al., Pubchem 2023 update, *Nucleic acids research* 51 (D1) (2023) D1373–D1380.
- [3] T. Jang, L. Mishra, K. Shah, A. Subramaniam, M. Uppaluri, S. A. Roberts, V. R. Subramanian, Towards real-time simulation of two-dimensional models for electrodeposition/stripping in lithium-metal batteries, *ECS Transactions* 104 (1) (2021) 131.
- [4] M. Plapp, Unified derivation of phase-field models for alloy solidification from a grand-potential functional, *Physical Review E* 84 (3) (2011) 031601.
- [5] V. Feyen, N. Moelans, Quantitative high driving force phase-field model for multi-grain structures, *Acta Materialia* 256 (2023) 119087.
- [6] J. Zhang, A. F. Chadwick, D. L. Chopp, P. W. Voorhees, Phase field modeling with large driving forces, *npj Computational Materials* 9 (1) (2023) 166.