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Electronic Supplementary Information: Dynamics and Morphology of Solid Electrolyte Interphase (SEI)†

Fabian Single,[a,b,‡] Birger Horstmann,*[a,b,‡] and Arnulf Latz [a,b,c]

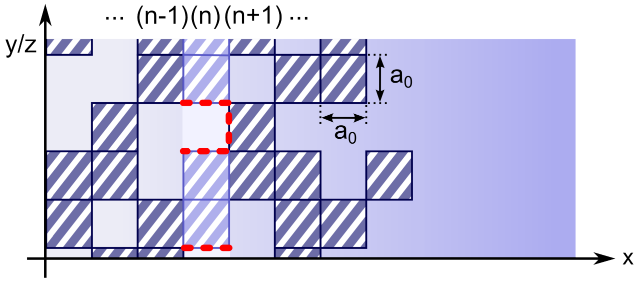

Fig. 1 Scheme for the derivation of eq (9). SEI is assumed to be constructed from cubes with volume a_0^3. The surface area for growth in slice (n) (dashed) is marked red and depends on the occupation probabilities of slice (n) as well as on occupation probability of the neighbouring slices $(n-1)$ and $(n+1)$.

Specific Surface Area

We derive an expression for the local specific surface area from the assumption that SEI consists of cubes with edge length a_0, as shown in Figure 1. All cubes in one slice (n) are occupied with the same probability, the local SEI volume fraction $\varepsilon_{\mathrm{SEI}}^{(n)} = 1 - \varepsilon^{(n)}$. In this way, the surface area in slice (n) also depends on the porosity of the neighbouring slices. This is approximated with the second derivative of ε

$$A_i = \frac{6}{a_0}\varepsilon\left(\tilde{\varepsilon} + \frac{a_0^2}{6}\frac{\partial^2\tilde{\varepsilon}}{\partial x^2}\right),$$

where $\tilde{\varepsilon}$ is the volume fraction of SEI compounds whose surfaces can facilitate SEI formation. We assume that SEI forms only on similar species as well as initial SEI, i.e. $\tilde{\varepsilon} = \varepsilon_i + \varepsilon_{\mathrm{init.}}$. The initial SEI profile is needed to start the simulation, providing a nucleation seed.

Boundary Conditions and Initialization

We initialize the system in equilibrium at $t = 0$. Thus, solvent concentration and electric potential equal the reference and equilibrium values c_{EC}^0 and Φ_{EC}^0 in the whole simulation domain. Both SEI volume fractions and the convective velocity are zero initially. A smooth initial profile $\varepsilon_{\mathrm{init}}$ serves as nucleation seed for SEI growth (see Figure 2(a)). Its thickness of 2 nm is interpreted as the electron tunneling depth through several SEI compounds[1]. Note that $\varepsilon_{\mathrm{init}}$ is zero for $x > 2\,\mathrm{nm}$. The electrode potential $\Phi(0,t)$ is determined by the state of charge (SOC) dependent potential of graphite electrodes[2]. We perform an initial charge at the rate C/20 from Φ_{EC}^0 to Φ_{final} corresponding to a linear ramp of SOC. Then SOC and potential $\Phi(0,t)$ on the left boundary are kept constant. The boundary conditions $j_{\mathrm{E}}(x_{\max}) = 0$, $j_{\mathrm{D,i}}(0) = v(0) = 0$ prevent electrons from leaving the simulation domain and solvent molecules from flowing into the electrode.

Parameters

If not stated elsewhere, parameters used in figures and the results discussed are listed in Table 1. We use the partial molar volumes $\bar{V}_i^{\mathrm{E}}$ of the pure solvents[3]. Γ was calculated from $\bar{V}_{\mathrm{Li_2EDC}}$ by assuming a cubic primitive cell. Initial concentrations c_{EC}^0 are chosen to represent a 3:7 mixture by volume. Equilibrium potentials are chosen to be 0.8 V[4] for EC and 0.3 V for DMC. This value is used because inorganic species are found below this voltage[5]. It is also close to the value of 0.25 V at which Zhang et al. found a transition in SEI properties[6]. The diffusion coefficient is chosen in the same order of magnitude as self-diffusion coefficients measured by Hayamizu et al.[7].

Methods

The system of equations (2)-(5) is solved in MATLAB using the implicit ODE15i function. All equations are discretized with the

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* Corresponding Author: *birger.horstmann@dlr.de*
[a] *German Aerospace Center (DLR), Institute of Engineering Thermodynamics, Pfaffenwaldring 38-40, 70569 Stuttgart, Germany*
[b] *Helmholtz Institute Ulm (HIU), Helmholtzstraße 11, 89081 Ulm, Germany*
[c] *Ulm University, Institute of Electrochemistry, Albert-Einstein-Allee 47, 89069 Ulm, Germany*
† Main file available: [Enter DOI].
‡These authors contributed equally to this work'

Table 1 List of simulation parameters, all potentials relative to the Li/Li$^+$ reduction pair.

Parameter	Description	Value	Unit
Φ^0_{EC}	EC reduction potential	0.8	V[8]
Φ^0_{DMC}	DMC reduction potential	0.3	V[8]
Φ_{final}	electrode potential during simulation	0.1	V
$\bar{V}^{\mathrm{E}}_{\mathrm{EC}}$	EC molar volume	66.7	$\mathrm{cm}^3/\mathrm{mol}$[3]
$\bar{V}^{\mathrm{E}}_{\mathrm{DMC}}$	DMC molar volume	84.2	$\mathrm{cm}^3/\mathrm{mol}$[3]
$\bar{V}^{\mathrm{S}}_{\mathrm{Li_2EDC}}$	$\mathrm{Li_2EDC}$ molar volume	56.8	$\mathrm{cm}^3/\mathrm{mol}$[9]
$\bar{V}_{\mathrm{LiMC}}$	LiMC molar volume	60.0	$\mathrm{cm}^3/\mathrm{mol}$[9]
D^0_{EC}	EC diffusion coefficient	10^{-6}	cm^2/s[7]
c^0_{EC}	EC concentration in bulk electrolyte	4.5	mol/l
a_0	pore-size and size of SEI particles	1.0	nm
Γ	suface site density	4.0	$\mu\mathrm{mol/m}^2$[9]
E_{A}	transition state energy	1.0	eV[10,11]

finite volume method. If κ vanishes ($\varepsilon_{\mathrm{SEI}} = 0$), eq (5) cannot be used to solve for the potential. For this reason, we add a small regularization parameter $\Delta\kappa = 0.05 \cdot \kappa^0$ to the effective conductivity in eq (6), mimicking electron jumps into the electrolyte. The spatial resolution used in our simulations is 0.5 Å which realizes the continuum limit.

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