

## Supporting Information:

### Properties of the Space Charge Layers Formed in Li-Ion Conducting Glass Ceramics

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## Thermodynamic Model

The theoretical model is based on the work of Stefanie Braun et al. and extended to a different set of parameters. In addition, the capacitance arising from the space charge is calculated based on the simulations for various bias potentials.

In order to understand the intricacies of the modelling approach, the underlying thermodynamic equations are presented together with the development of the final one-dimensional equation for charge carrier concentrations at the interface layers in solid electrolytes. In particular, the boundary condition equations are reviewed and occurring singularities explained in detail.

To describe the lattice structure with a fixed anion lattice and mobile cation charges, the following parameters are introduced to describe the properties for a lattice position (*v:vacancy, a:anion, c:cation*) : *mass*  $m_\alpha$ , *charge*  $z_\alpha$ , *density*  $n_\alpha$ . Under the assumption of Mott-Schottky vacancies, the vacancies neither possess a mass nor a charge:  $m_v = 0, z_v = 0$ , justified by the vanishing energy of free vacancies. The lattice structure defines a free charge concentration  $n^F = \sum_{\alpha=v,a,c} z_\alpha n_\alpha$  with limits of  $z_c(n_c + n_v) \leq n^F \leq z_a n_a$ .

The basis of the thermodynamic model is built on the following equations:

$$\begin{aligned} \partial_t n_\alpha + \text{div}(n_\alpha v_\alpha) &= \partial_t n_\alpha + \text{div}\left(\frac{\rho}{\rho - \rho_\alpha} J_\alpha\right) = 0, \quad \alpha = v, c, a \\ -n^F \Delta \phi &= \partial_t(\rho v) + \text{div}(\rho v \otimes v) + \nabla p \\ n^F &= \text{div}(\epsilon_0 \epsilon_r E + P) \end{aligned}$$

The free charge carrier concentration  $n^F$  is the most important variable here, as it directly measures the charge distribution. The free energy functional used by Braun et al. contains polarization, linear elastic and entropy mixing contributions and combined with a positive entropy production rate and the chemical potentials yields a closed system of equations. A single one-dimensional equation with dimensionless variables can be derived, describing the space charge occurrence in the continuum model.

$$-n^F = \lambda^2 (F(n^F) \partial_{zz} n^F + (\partial_z F(n^F) (\partial_z n^F)^2))$$

The definition of  $F(n^F)$  and the derivation of the boundary conditions can again be found in the original article.

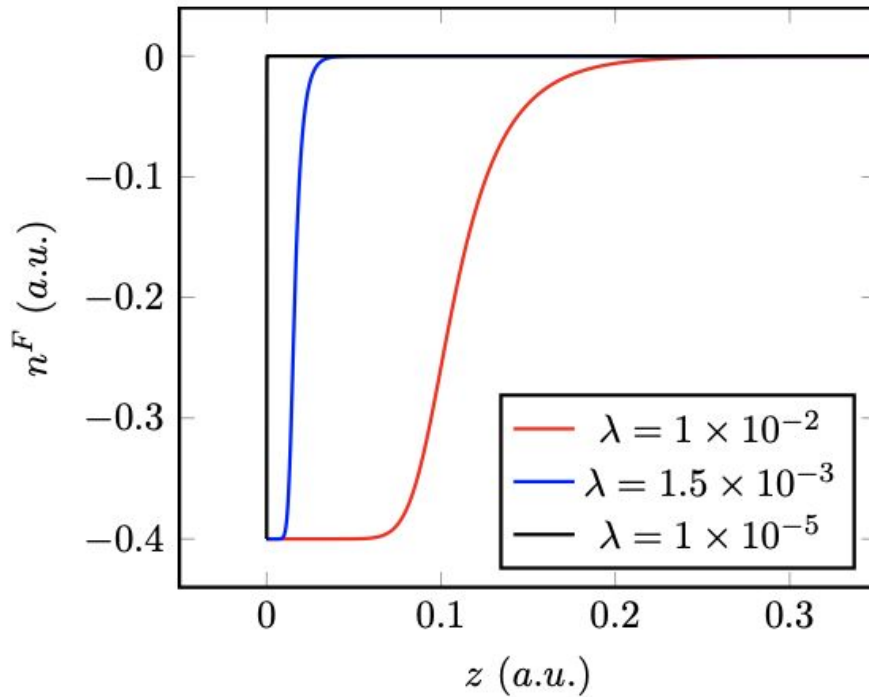
Remarkably, the boundary conditions, primarily dependent on the bias potential, are represented by the free charge carrier concentration at either end of the electrolyte. The function  $F(n^F)$  only contains the

maximum and minimum of charge carrier concentration (i.e.  $n_a, n_v$ ) whereas the parameter

$$\lambda = \frac{k_B T \epsilon_0 (1 + \chi)}{e_0^2 n^R (L^R)^2}$$

similar to the Debye-length in fluids, contains all other variables. Here, Boltzmann constant  $k_B$ , Temperature  $T$ , permittivity  $\chi$ , vacuum dielectric constant  $\epsilon_0$ , cation density in reference system  $n^R$ , and the characteristic length scale  $L^R$  are used.

Based on the space charge thickness given by this work, we calculated the space charge layer capacitances forming around the layer using  $C_{SCL} = \frac{\epsilon_R \epsilon_0 A}{d_{SCL}}$ . As the model yields dimensionless variables and the parameters for a back-transformation are not available, only a qualitative



behavior of the space charge capacitance can be determined.

Figure S1: Lambda variation shows strong influence on space charge layer depth, implying a direct influence of temperature and cation density on the formation.

The thickness of the space charge layer is directly proportional to the square of the characteristic length  $\lambda$  as observable in Figure S1. Due to the incomplete parameterization, i.e. the missing charge carrier density, a qualitative analysis of the theoretical model is not possible. However, the quantitative behavior does not change when the parameters are incompletely defined.

**Equivalent Circuit Parameter for Different Metal Electrodes.**

<i>Electrode:</i>	<i>Au</i>		<i>Cr</i>		<i>Au/Ti</i>		<i>Unit</i>
	Value	Error	Value	Error	Value	Error	
$C_{GEOM}$	3.74E-09	1.10E-10	3.53E-09	1.16E-10	3.82E-09	1.60E-10	[F/cm <sup>2</sup> ]
$C_{SCL}$	1.22E-05	1.85E-06	2.40E-05	4.80E-06	6.68E-06	1.65E-06	[F/cm <sup>2</sup> ]
$R_U$	16.73	0.45	21.77	0.53	16.18	0.92	[Ohm]
$R_B$	55.87	0.77	60.85	0.87	57.59	1.14	[Ohm]
$R_{SCL}$	6319.42	3963.79	1353	718.17	22.05	1.82	[Ohm]
$R_{LEAK}$	1.52E+06	6.46E+05	5.53E+05	2.08E+05	4.01E+07	1.48E+07	[Ohm]
$C'_{DL}$	1.14E-06	1.07E-08	3.03E-06	3.04E-08	7.56E-06	1.14E-07	[F/cm <sup>2</sup> ]
$\alpha_{DL}$	0.97	1.57E-03	0.90	1.80E-03	0.93	3.12E-03	

Table S1: Equivalent circuit parameters for different metal electrodes.