DOUBLE LAYER NONDIMENSIONALIZATION

We *briefly* derive the nondimensionalized evolution equation for the solid-electrolyte overpotential for a DFN model.

1. Notational conventions

I will adopt the notational convention for dimensional/nondimensional variables from [1]. In brief, hats will denote dimensional variables while no-hats will denote nondimensional variables. Additionally, we make the distinction if i as a through-cell current density and j as a pore-wall current density.

2. Dimensional equation

We begin with the equations describing:

- total pore-wall current density as the sum of Faradaic and non-Faradaic current densities,
- non-Faradaic current density expressed via double layer capacitance,
- conservation of charge in electrolyte,

given respectively by

$$\begin{aligned} \widehat{j}_{\text{total}} &= \widehat{j}_f + \widehat{j}_{nf}, \\ \frac{\partial \widehat{\phi}}{\partial \widehat{t}} &= \frac{1}{\widehat{C}} \widehat{j}_{nf}, \\ \widehat{\nabla} \cdot \widehat{i}_e &= \widehat{a} \widehat{j}_{\text{total}}. \end{aligned} \tag{1}$$

Here $\widehat{j}$ denotes the various components of the pore-wall current density [Am^{-2}], $\widehat{\phi}$ denotes the solid-electrolyte overpotential [V], $\widehat{i}_e$ denotes the current density in the electrolyte [Am^{-2}], $\widehat{C}$ denotes the double layer capacitance [Fm^{-2}], and $\widehat{a}$ denotes the specific surface area [m^{-1}]. Combining the equations in (1) we arrive at the *dimensional* PDE describing the change in the solid-electrolyte overpotential:

$$\frac{\partial \widehat{\phi}}{\partial \widehat{t}} = \frac{1}{\widehat{a}\widehat{C}} \left(\widehat{\nabla} \cdot \widehat{i}_e - \widehat{a} \widehat{j}_f \right). \tag{2}$$

3. Nondimensionalization

For all dimensional variables, we assume the following dimensional scaling:

$$\widehat{y} = y_0 y,$$

where $\widehat{y}$ denotes the dimensional variable, y_0 denotes the characteristic dimension (i.e., the scaling value), and y denotes the *dimensionless* variable. Performing the appropriate variable substitutions in (2) we find

$$\frac{\partial \phi_0 \phi}{\partial t_0 t} = \frac{1}{a_0 a C_0 C} \left(\frac{1}{x_0} \nabla \cdot (i_0 i_e) - a_0 a j_0 j_f \right). \tag{3}$$

Then collecting all dimensional scalings to the right-hand side of the equation we arrive at

$$\frac{\partial \phi}{\partial t} = \frac{t_0 i_0}{\phi_0 a_0 C_0 x_0} \frac{1}{aC} \left(\nabla \cdot i_e - \frac{x_0 a_0 j_0}{i_0} a j_f \right). \tag{4}$$

4. Dimensional scalings in PyBaMM

Looking through the source code and referring again to [1], we find the dimensional scalings as in Table 1 If we plug these values into (4) we find

Variable	Value
i_0	i_{typ}
t_0	$Fc_{\max} L_x / i_{\text{typ}}$
a_0	a_{typ}
x_0	L_x
j_0	$i_{\text{typ}} / (a_{\text{typ}} L_x)$
C_0	$j_0 t_0 / \phi_0$
ϕ_0	RT/F

Table 1. Dimensional scalings in PyBaMM for a standard DFN model.

$$\begin{aligned}
\frac{\partial \phi}{\partial t} &= \frac{\cancel{t_0} i_0}{\cancel{\phi_0} a_0 \frac{j_0 \cancel{t_0}}{\cancel{\phi_0}} x_0} \frac{1}{aC} \left(\nabla \cdot i_e - \frac{x_0 a_0 j_0}{i_0} a j_f \right) \\
&= \frac{i_0}{a_0 j_0 x_0} \frac{1}{aC} \left(\nabla \cdot i_e - \frac{x_0 a_0 j_0}{i_0} a j_f \right) \\
&= \frac{i_{\text{typ}}}{a_{\text{typ}} \frac{i_{\text{typ}}}{a_{\text{typ}} L_x} L_x} \frac{1}{aC} \left(\nabla \cdot i_e - \frac{L_x a_{\text{typ}} \frac{i_{\text{typ}}}{a_{\text{typ}} L_x}}{i_{\text{typ}}} a j_f \right) \\
&= \frac{1}{aC} \left(\nabla \cdot i_e - a j_f \right).
\end{aligned} \tag{5}$$

When comparing this final equation with the expression shown here (link), we find a missing scaling of $1/a$.

Remark 1 (Spatially-uniform particle sizes and active material volume fraction)**.** *In the often-used assumption of a spatially-uniform distribution of particle sizes and active material volume fractions throughout the DFN model, we have $\widehat{a} \equiv a_{typ}$ and thus $a \equiv 1$. Therefore, with this assumption the expression used in PyBaMM for the overpotential dynamics remains valid. However, to the best of our understanding, if there is a situation where the particle sizes and/or active material volume fraction is allowed to spatially vary, it seems the expression needs to be corrected by including the scaling factor of $1/a$.*

References

[1] V. Sulzer, S. J. Chapman, C. P. Please, D. A. Howey, and C. W. Monroe. Faster Lead-Acid Battery Simulations from Porous-Electrode Theory: Part I. Physical Model. *Journal of The Electrochemical Society*, 166(12):A2363–A2371, 2019. ISSN 0013-4651, 1945-7111. doi: 10.1149/2.0301910jes. URL `https://iopscience.iop.org/article/10.1149/2.0301910jes`.