A homogenization study of the effects of cycling on the electronic conductivity of commercial lithium-ion battery cathodes: Supporting information

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Rigorous bounds on the effective conductivity

In this appendix we discuss rigorous bounds on the effective conductivity $\boldsymbol{\sigma}^*$. These bounds will be used to give perspective on how well the cathodes perform relative to optimal geometric configurations. First, we will discuss the elementary (Weiner) bounds for a three phase material (with only two distinct length scales) that can be homogenized in a single step. We will then demonstrate how these elementary bounds can be improved (tightened) for a three-phase material with three distinct length scales using the nested homogenization procedure presented here.

Bounds on $\boldsymbol{\sigma}^*$ for homogenization performed in a single step. Rigorous bounds on the effective electronic conductivity for a three phase material with two distinct length scales can be found in [8]. Examples of such materials are the cathodes that we have studied here, but without the extremely small scale electrolyte pores — recall that it is the presence of these electrolyte pores that motivated us to develop the nested homogenization procedure. We have

$$\left(\frac{p_B}{\sigma_B}+\frac{p_{AP}}{\sigma_{AP}}+\frac{p_E}{\sigma_E}\right)^{-1} \leq \sigma^* \leq p_B\sigma_B + p_{AP}\sigma_{AP} + p_E\sigma_E =: \sigma_A. \tag{1}$$

Here p_B, p_{AP}, and p_E, σ_B, σ_{AP}, and σ_E, are the volume fractions (taken with respect to the whole sample) and electronic conductivities of the binder, active material and electrolyte phases, respectively.

Bounds on $\boldsymbol{\sigma}^*$ for nested homogenization. As discussed, when a three-phase material exhibits three distinct length scales (*e.g.* the cathodes studied here), a nested homogenization procedure can be employed. As we will show, applying the elementary bounds in this same nested fashion can yield tighter bounds on the conductivity of the whole material. First, consider applying the elementary bounds to first stage of the homogenization over the smallest length scale, *i.e.* (a)(i)→(b) and (a)(ii)→(b) shown in figure 3, which yields the values of the effective combined phase conductivities

$\sigma^*_{AP/E}$ and $\sigma^*_{B/E}$. Applying the elementary bounds to these steps we have:

$$\left(\frac{\tilde{p}_{AP}}{\sigma_{AP}} + \frac{\tilde{p}_E}{\sigma_E}\right)^{-1} \leq \sigma^*_{AP/E} \leq \tilde{p}_{AP}\sigma_{AP} + \tilde{p}_E\sigma_E, \tag{2}$$

$$\left(\frac{\hat{p}_B}{\sigma_B} + \frac{\hat{p}_E}{\sigma_E}\right)^{-1} \leq \sigma^*_{B/E} \leq \hat{p}_B\sigma_B + \hat{p}_E\sigma_E. \tag{3}$$

Here $\tilde{p}_{AP}$ and $\tilde{p}_E$ are the volume fractions of the active material and electrolyte taken with respect to the active material/electrolyte combined phase subsample (panel (a)(i) in figure 3), whereas $\hat{p}_B$ and $\hat{p}_E$ are the volume fractions of binder and electrolyte taken with respect to the binder/electrolyte combined phase subsample (panel (a)(ii) in figure 3).

Now consider the second stage of the homogenization over the intermediate length scale, *i.e.*, step (b)→(c) in figure 3, which yields the effective conductivity of the whole sample. We have

$$\left(\frac{\bar{p}_{B/E}}{\sigma^*_{B/E}} + \frac{\bar{p}_{AP/E}}{\sigma^*_{AP/E}} + \frac{\bar{p}_E}{\sigma_E}\right)^{-1} \leq \sigma^* \leq \bar{p}_{B/E}\sigma^*_{B/E} + \bar{p}_{AP/E}\sigma^*_{AP/E} + \bar{p}_E\sigma_E =: \sigma_B. \tag{4}$$

Here, $\bar{p}_{B/E}$, $\bar{p}_{AP/E}$ and $\bar{p}_E$ are the volume fractions of the combined active material/electrolyte phase, the combined binder/electrolyte phase and the electrolyte taken with respect to the whole sample (panel (b) in figure 3).

We now note that the volume fractions of the individual phases in the whole sample are related to the hatted, overbarred and tilded volume fractions via:

$$p_{AP} = \bar{p}_{AP}\ \tilde{p}_{AP}, \tag{5}$$

$$p_B = \bar{p}_{B/E}\ \hat{p}_B, \tag{6}$$

$$p_E = \bar{p}_E + \bar{p}_{AP/E}\ \tilde{p}_E + \bar{p}_{B/E}\ \hat{p}_E. \tag{7}$$

On: (i) inserting the elementary bounds for the active material/electrolyte and binder/electrolyte combined phases, (2) and (3), into (4); (ii) rearranging, and; (iii) relating the hatted, overbarred and tilded volume fractions to those used in (1) (via (5)–(7)), we see that the nested homogenization bounds, (4), are tighter than those derived by directed homogenization, (1), *i.e.*, we have $\sigma_B < \sigma_A$, provided that none of the volume fractions are zero — which is certainly the case here. The bounds

(2)–(4) are used to provide perspective on how large the effective electronic conductivities reported in tables 3 and 4 are with respect to their maximum values.