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University College Cork, Ireland Coláiste na hOllscoile Corcaigh Supporting Information for

Quantifying the effect of electronic conductivity on the rate-performance of nanocomposite battery electrodes

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Electrode density



Figure S1: Electrode density versus filler content.



Galvanostatic charge discharge curves

Figure S2: Second cycle charge-discharge curves for electrodes of NMC811 filled with different loadings of A) graphene, B) carbon nanotubes and C) carbon black. All measurements were performed at I/A=17 mA/g.

Calculating the curve in figure 5B

We can plot equation 6a on figure 5B as follows.

Equation 6a can be written as:

$$\frac{\tau}{L_E^2} = \frac{14Q_V}{\sigma_{OOP}} + \left[\frac{28Q_V}{2\sigma_{BL}P_E^{3/2}} + \frac{1}{D_{BL}P_E^{3/2}} + \frac{L_S}{L_E}\frac{28Q_V}{\sigma_{BL}P_S^{3/2}} + \frac{1}{L_E^2}\left(\frac{L_S^2}{D_{BL}P_S^{3/2}} + \frac{L_{AM}^2}{D_{AM}} + t_c\right)\right]$$

When plotted as τ / L_E^2 vs. Q_V / σ_{OOP} the expected slope is 14 F/mAh while the intercept is the set of terms in the square brackets. The intercept can be found when $1/\sigma_{OOP}=0$ or when $\sigma_{OOP}\rightarrow\infty$.

For illustrative purposes, we plot τ / L_E^2 vs. σ_{OOP} below. The intercept in figure 5B is the constant value of τ / L_E^2 when σ_{OOP} becomes large. To plot this, we need to estimate the relevant parameters:

$\langle Q_V \rangle = 2.1 \times 10^8 \text{ mAh/m}^3$	Found using $Q_V = \rho_E Q_M$ and averaging over all samples.
σ_{BL} =0.5 S/m	Typical for LIB electrolytes ¹
$D_{BL}=3\times 10^{-10} \text{ m}^2/\text{s}$	Middle of the range for common battery electrolytes ²⁻³
P _E =0.6	Estimated from mean electrode density
P _S =0.4	Typical for commercial separators ⁴
L _S =16 μm	Celgard 2032 separator
$\langle L_E \rangle = 97 \ \mu m$	Measured mean thickness
$L_{AM}=r/3\sim 2\mu m$	Proposed relationship between L_{AM} and particle radius ⁵
$D_{AM}=5\times10^{-14} \text{ m}^2/\text{s}$	Diffusivity of Li ions in NMC111 ⁶
t _c =25s	Roughly middle of the range reported by ⁵

Using these parameters yields the following graph which clearly shows the limiting value to be 3.5×10^{10} s/m².



Figure S3: Calculating τ / L_E^2 versus OOP conductivity.



Figure S4: Critical (out-of-plane) electrode conductivity, $\sigma_{OOP,min}$, plotted as a function of electrode thickness (L_E) and low rate volumetric capacity (Q_V). The critical conductivity is that required to reduce the contribution to τ associated with the electrode resistance (first term in equation (6a)) below 10% of the sum of the other contributions to τ (i.e. the other six terms in equation (6a)). Here we calculate $\sigma_{OOP,min}$ using the following parameters: $\langle Q_V \rangle = 2.1 \times 10^8$ mAh/m³, $\sigma_{BL}=0.5$ S/m, $D_{BL}=3\times 10^{-10}$ m²/s, $P_E=0.6$, $P_S=0.4$, $L_S=16$ µm, $\langle L_E \rangle = 97$ µm. In A and

B, this calculation is performed for electrode materials with long (A, τ_{SSD} +t_c=10⁴s) and short

(B, $\tau_{SSD}+t_c=1s$) combinations of solid-state diffusion and reaction times.

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