Quantitative characterization of the ionic mobility and concentration in Li-battery cathodes via Low Frequency Electrochemical Strain Microscopy

D.O. Alikin\textsuperscript{a,b,‡,*}, K.N. Romanyuk\textsuperscript{a,b,‡}, B.N. Slautin\textsuperscript{a}, D. Rosato\textsuperscript{c}, V.Ya. Shur\textsuperscript{a} and A.L. Kholkin\textsuperscript{a,b}

\textsuperscript{a}School of Natural Sciences and Mathematics, Ural Federal University, 620000 Ekaterinburg, Russia
\textsuperscript{b}Department of Physics & CICECO – Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal
\textsuperscript{c}Robert Bosch GmbH, 70839 Gerlingen-Schillerhoehe, Germany
\textsuperscript{‡}equal contribution

Supplementary Information

A.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{current_voltage_characteristics}
\caption{Current-voltage characteristics in PVDF binder mixed with carbon black for the different applied forces.}
\end{figure}

B.

In spherically symmetrical approach electrical impedance for semispace can be estimated as

\[ R = 2\int_{a}^{\infty} \frac{\rho(r) \cdot dr}{4\pi r^2} \]  \quad (S1)
and $\rho(r)$ is electrical resistivity.

Using “model” distribution (see Fig. 5 in the paper) with two regions: with original resistivity $\rho_0 = \frac{1}{q\mu_e C_0}$ and increased resistivity $\rho_1 = \frac{1}{q\mu_e C_1}$, here $\mu_e$ is the electron mobility, $q$ is elementary charge, $C_0$ and $C_1$ are electron concentrations at the step-like concentration profile (Fig. 6 in the paper) which are equal to the ionic concentration due to neutrality conditions $C_{Li} \approx C_e$. The impedance for semispace can be estimated as:

\[ R \approx \frac{\rho_1}{2\pi} \left( \frac{1}{a} - \frac{1}{r} \right) = \frac{1}{2\pi q\mu_e C_1} \left( \frac{1}{a} - \frac{1}{r} \right), \]  

(S2)

here $a$ is contact radius, in the case of $\rho_0 \ll \rho_1$ it simplifies to:

\[ R \approx \frac{\rho_1}{2\pi} \left( \frac{1}{a} - \frac{1}{r} \right) \]  

then $I(C(r,t)) = U_{\text{eff}} 2\pi q\mu_e C_1 \left( \frac{1}{a} - \frac{1}{r} \right)^{-1}$ and

\[ E_e(r) = \frac{U_{\text{eff}} 2\pi q\mu_e C_1 \left( \frac{1}{a} - \frac{1}{r} \right)^{-1}}{2\pi^2 q\mu_e \cdot C(r,t)} = \frac{U_{\text{eff}} C_1}{r^2 C(r,t) \left( \frac{1}{a} - \frac{1}{r} \right)}, \]  

at $a \ll r$ it simplifies to

\[ E_e(r) = \frac{a U_{\text{eff}} C_1}{r^2 C(r,t)}. \]  

(S4)

C.

According with S3 maximal electric impedance for positive voltage (“model” distribution at Fig. 5 in the body of paper) can be estimated at $a \ll r$ as: $R_1 \approx \frac{1}{2\pi q\mu_e C_1}$ and electric impedance for negative voltage $R_0 \approx \frac{1}{2\pi q\mu_e C_0}$. Using $\tilde{C}_1$ instead of $C_1$ we find that

\[ \frac{R_1}{R_0} \approx \frac{C_0}{\tilde{C}_1}. \]  

(S5)
From current-voltage characteristics and using relation S5 we estimated \( \frac{C_0}{C_1} \sim 3 \).