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

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Supplementary Information

A.

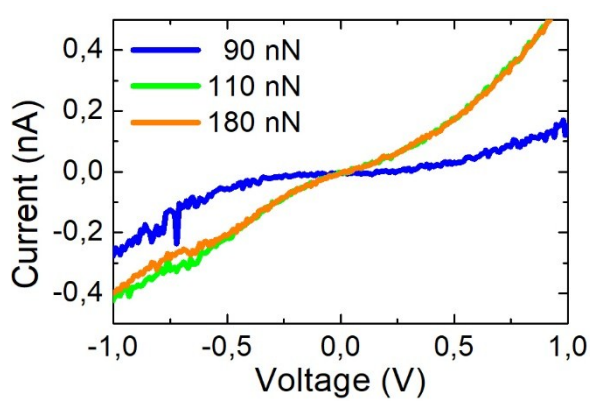

Figure S1. Current-voltage characteristics in PVDF binder mixed with carbon black for the different applied forces.

B.

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

$$R = 2\int_{a}^{\infty} \frac{\rho(r)\cdot dr}{4\pi r^2} \tag{S1}$$

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 μ_{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:

, (S2)

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

$$R \approx \frac{\rho_1}{2\pi}\left(\frac{1}{a}-\frac{1}{r}\right) = \frac{1}{2\pi q\mu_{e^-}C_1}\left(\frac{1}{a}-\frac{1}{r}\right), \tag{S3}$$

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

$$E_r(r) = \frac{U_{eff}\, 2\pi q\mu_{e^-}C_1\left(\frac{1}{a}-\frac{1}{r}\right)^{-1}}{2\pi r^2 q\mu_{e^-}\cdot C(r,t)} = \frac{U_{eff}C_1}{r^2C(r,t)\left(\frac{1}{a}-\frac{1}{r}\right)}$$, at $a << r$ it simplifies to

$$E_r(r) = \frac{aU_{eff}C_1}{r^2C(r,t)}. \tag{S4}$$

C.

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

$$\frac{R_1}{R_0} \approx \frac{C_0}{\tilde{C}_1}. \tag{S5}$$

From current-voltage characteristics and using relation S5 we estimated $\frac{C_0}{\tilde{C}_1} \sim 3$.