Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting information

Modelling of the heterogenous ion transport in conducting polymer supercapacitors

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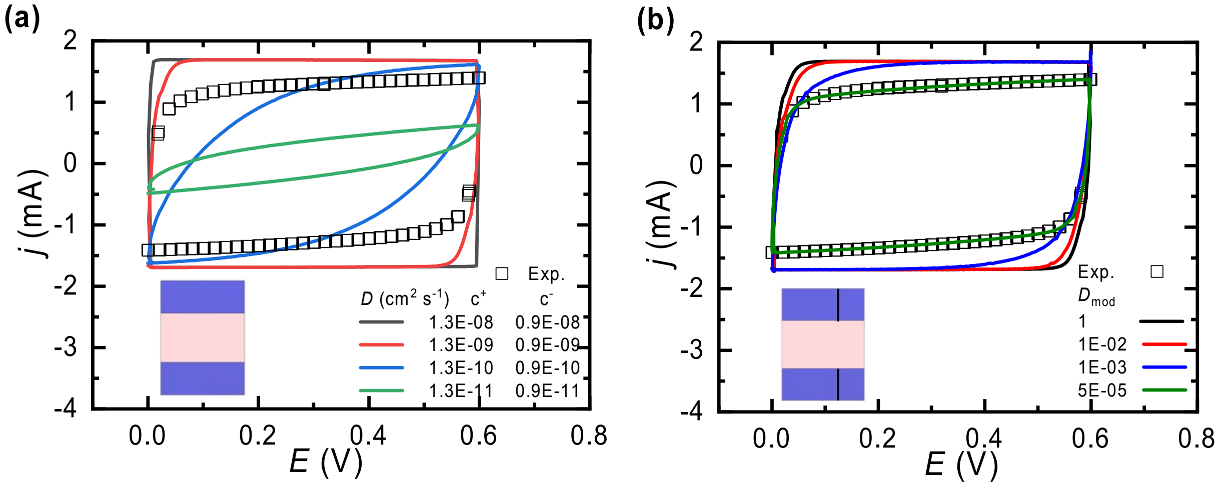

Fig. S1: Attempts to reproduce experimental (Exp.) CV results at 10 mV/s. (a) For the homogeneous model the effective cation and anion diffusivities within the electrode are varied. (b) Using the heterogeneous model; by reducing effective cation and anion diffusivity in ~27 % of electrode domain (right portion, see inset) by factor , while keeping 1.3 E-09 and 0.9 E-09 as cation and anion diffusivity respectively in the remaining (~63 %) of the electrode domain.

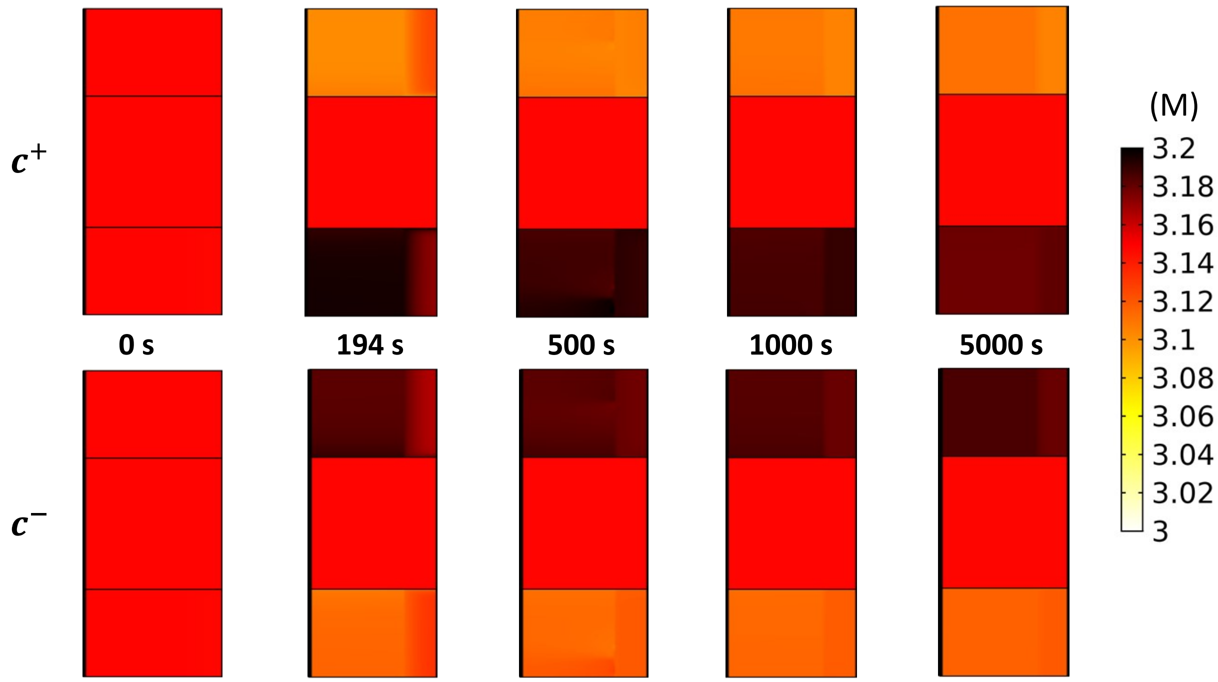

Fig. S2: Evolution of cation and anion concentration (in molar) during self-discharge tests simulated by the heterogeneous model including ORR. 0 s: Charging starts at 100 mA/g. 194 s: Charging cut-off potential is reached, switch to open circuit potential measurement. 500 s: halfway through ion redistribution. 1000 s: majority of ion redistribution has occurred. 5000 s end of test. Positive electrode on top, negative below.

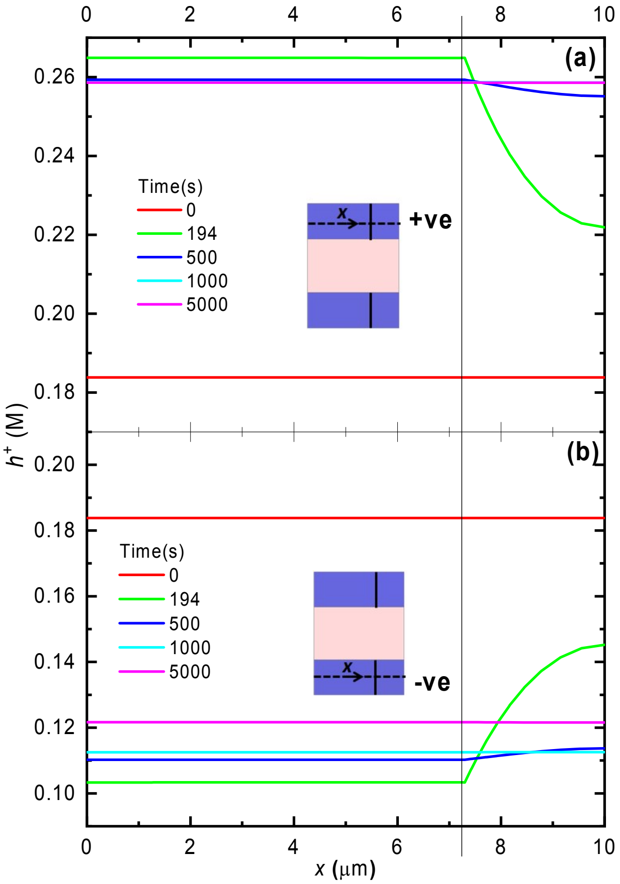

Fig. S3: Transition of spatial hole concentration along both electrode lateral centre lines (as shown inset - in molar), at critical times during self-discharge tests produced by the heterogeneous model including ORR. 0 s: Charging starts at 100 mA/g. 194 s: Charging cut-off potential is reached, switch to open circuit potential measurement. 500 s: mid-way of ion redistribution. 1000 s: after majority of ion redistribution. 5000 s end of test. Positive electrode on top, negative below.

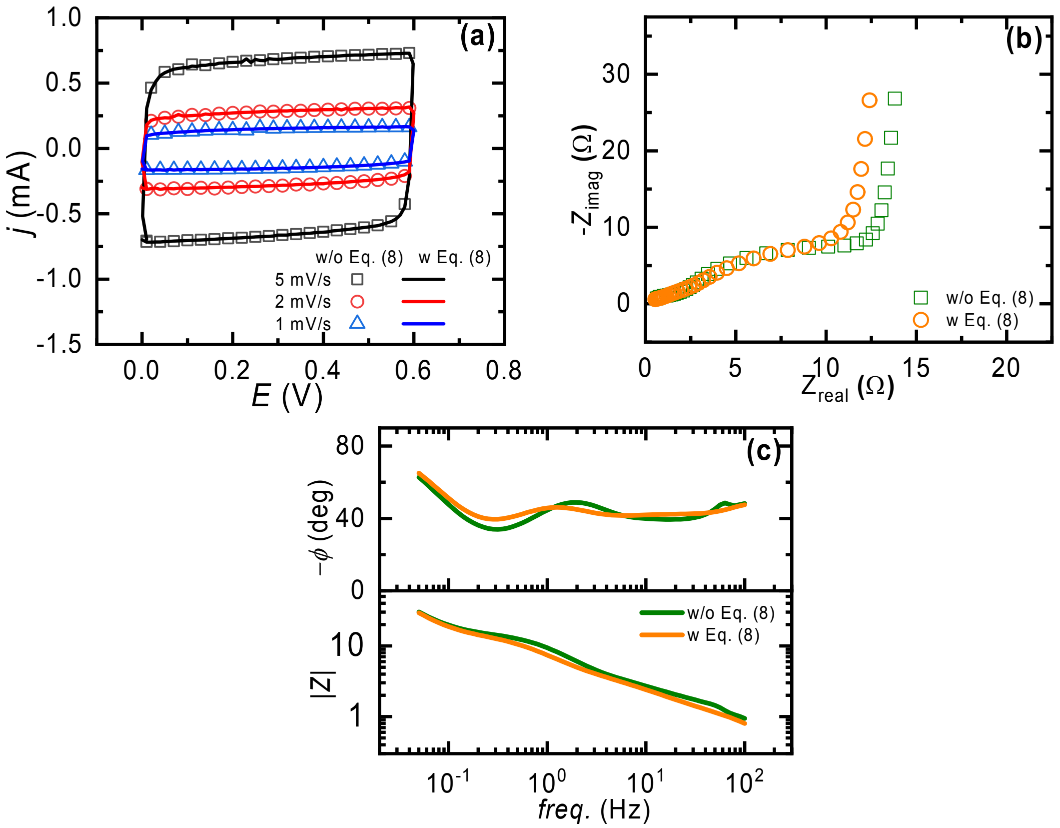

Fig. S4: Comparison of real model results with or without (w. or w/o.) Equation 8 (Eq. 8): (a) Steady-state cyclic voltammograms at lower scan rates. (b) Nyquist plot from EIS simulation. (b) Bode plots from EIS simulation. EIS is simulated at 0 V with 10 mV perturbation.

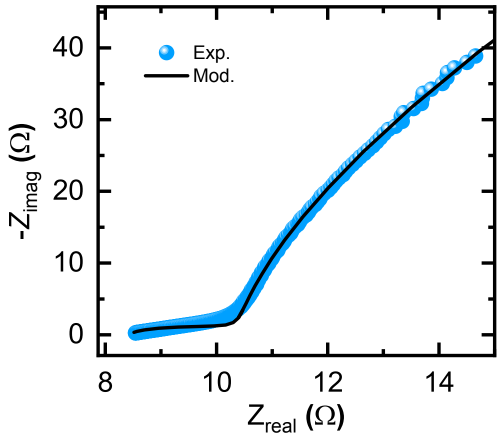

Fig. S5: Nyquist plot of experimental CPSC data and the fitted model. The model fits the data well within the 100 Hz to 50 mHz frequency range. The experimental data is from a different batch of CPSCs than the data used in the rest of the manuscript. A contact resistance was added to the model to account for the contact resistance between the current collector and the CP electrodes.

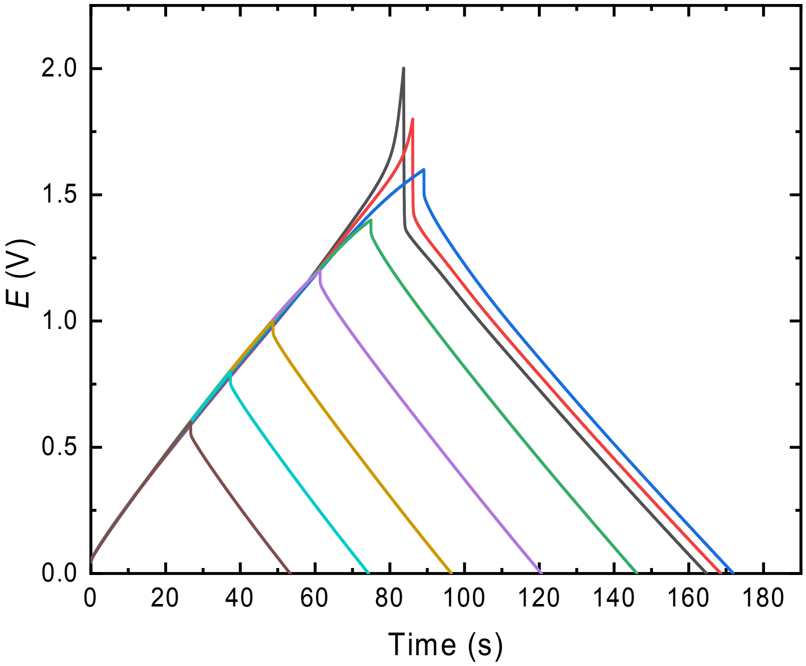

Fig. S6: Experimental charge-discharge at 700 mA/g with varying cut-off potential from 0.6 to 2 V in 0.2 V steps.

Table S1: Nominal operating parameters and variables for the model.

Description	**Electrode Domains**	**Separator Domain**
D_{h^+} **(cm^{2}s^{-1})** [1]	$0.205\left(0.93 - \frac{1.1}{1 + exp\left(\frac{(h^{+} - 71)}{23}\right)}\right)$	-
D_{c^+} **/** D_{c^-} **(cm^{2}s^{-1})**	1.3E-9 / 0.9E-9 high 6.5E-14 / 4.5E-14 low	1.0E-9 / 0.7E-9^{++}
$v_{f,i}$	0.23 for ions 0.67 for holes	0.85*
ε	28 for ions [2] 40 for holes [1]	28
C_v **(mol/(m^{3}V))**	291 [3]	-
c_{fix} **(M)**	0.18	-
k_0 **(s^{-1})**	1.6E-5	

*From manufacturer manual. – Not applicable. ++ Bruggeman porosity correction of values from Mao. et. al. [4].

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