

Supplementary Material: Understanding Resistances in Capacitive Deionization Devices

Helen A. Kuo,[†] Ashwin Ramachandran,[‡] Diego I. Oyarzun,[†] Erica C. Clevenger,[†]
Juan G. Santiago,[¶] Michael Stadermann,[†] Patrick G. Campbell,[†] and Steven A.
Hawks^{*,†}

[†]*Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550, United States*

[‡]*Department of Aeronautics & Astronautics, Stanford University, Stanford, CA 94305, United
States*

[¶]*Department of Mechanical Engineering, Stanford University, Stanford, CA 94305, United States*

E-mail: hawks3@llnl.gov

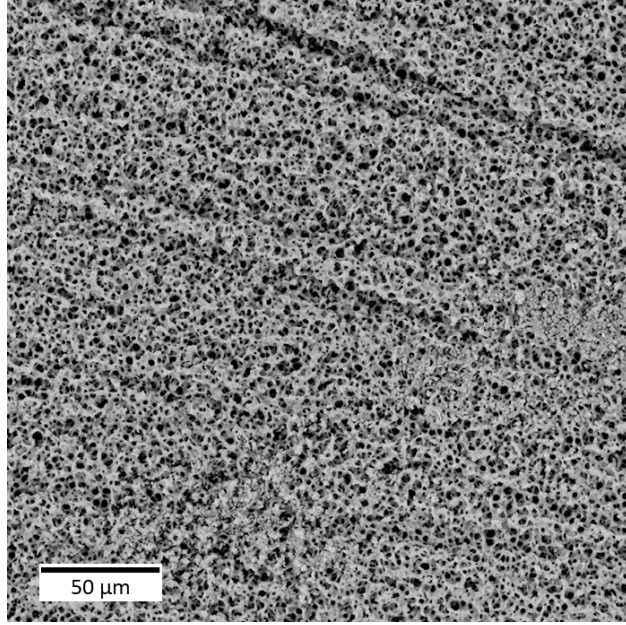


Figure S1: A SEM image of activated HCAM electrode material. The image shows the 355 μm thick electrode.

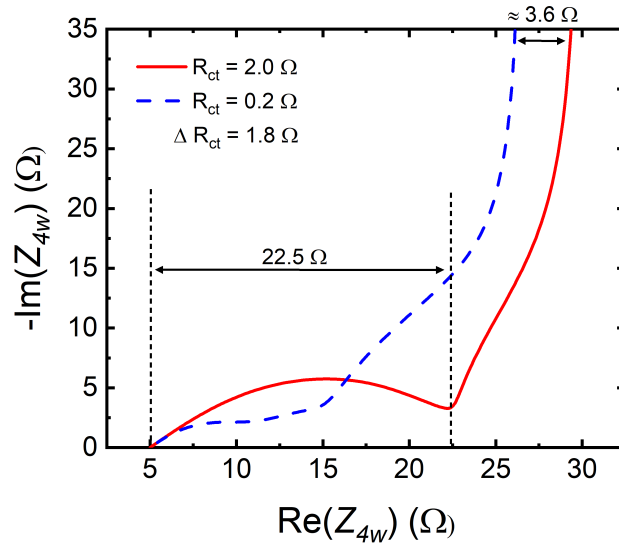


Figure S2: Calculated impedance of an EIS cell with $R_{iER} + R_{SP} = 5 \Omega$, $R_{st} = 2 \Omega$, $\tau_{st} = 12 \text{ s}$, $R_{mA} = 30 \Omega$, $C_w = 0.15$, $n = 0.5$, and R_{ct} as shown. Though the arc at low frequencies grows drastically with an increase in charge transfer resistance, the total cell resistance R_{4w} only increases by $2R_{ct}$ as predicted by the model (the factor of 2 comes from the fact that there are two electrodes).

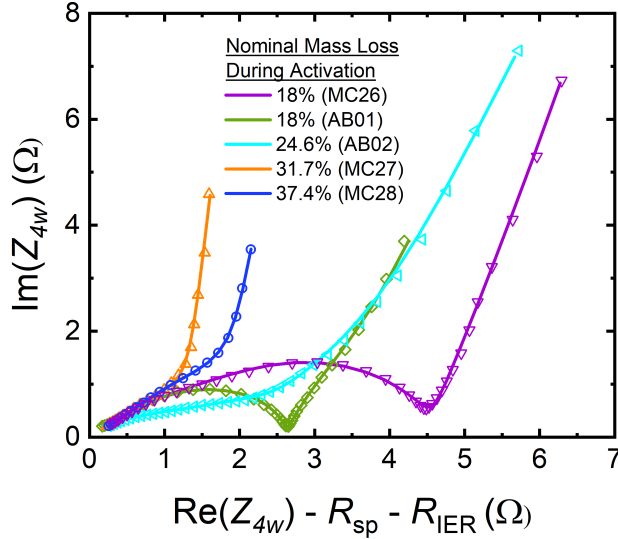


Figure S3: EIS spectra from 4×5.6 cm two electrode cells in 20mM NaCl with fits from Eqns (3-5). Open symbols are experimental data and lines are fits. The cells were assembled from HCAM electrodes with different levels of activation, measured as mass loss. R_{ct} values from the fits were less than 0.1Ω for all but the 18% activation samples and the charge transfer is not visible for the higher activation samples.

Table S1: Impedance Fitting Parameters

	$R_{sp} + R_{IER}$ (Ω)	R_{mA} (Ω)	C_w (F)	R_{ct} (Ω)	R_{st} (Ω)	τ_{st} (s)	n
50 mM NaCl	1.11 ± 0.03	7.6 ± 0.2	0.12	0.05 ± 0.05	0.10 ± 0.04	0.87 ± 0.38	0.42 ± 0.01
100 mM NaCl	0.62 ± 0.08	3.9 ± 0.3	0.12	0.03 ± 0.03	0.06 ± 0.05	0.61 ± 0.51	0.43 ± 0.01
200 mM NaCl	0.37 ± 0.07	2.3 ± 0.1	0.15	0.01 ± 0.04	0.05 ± 0.06	0.73 ± 0.92	0.46 ± 0.01
500 mM NaCl	0.20 ± 0.05	1.1 ± 0.1	0.19	0.005 ± 0.03	0.03 ± 0.05	0.65 ± 0.91	0.49 ± 0.01
2000 mM NaCl*	0.09 ± 11.0	$3 \times 10^{-5} \pm 16$	0.006	0.03 ± 0.14	0.33 ± 0.01	7.7 ± 0.3	0.49 ± 0.01
15 mM NaF	3.85 ± 0.09	38 ± 7	0.15	0.90 ± 0.18	3.0 ± 0.5	13.5 ± 3.8	0.38 ± 0.02
15 mM NaBr	3.27 ± 0.04	23 ± 2	0.14	0.54 ± 0.05	1.3 ± 0.1	9.1 ± 1.3	0.38 ± 0.01
15 mM NaCl	3.33 ± 0.04	29 ± 4	0.16	0.76 ± 0.12	1.3 ± 0.2	8.1 ± 2.2	0.39 ± 0.01
18% act cell 1*	3.4 ± 0.2	2.8 ± 1.0	0.037	1.4 ± 1.7	0.25 ± 0.08	0.4 ± 22	0.42 ± 0.01
18% act cell 2*	1.17 ± 0.05	4.1 ± 0.7	0.041	0.4 ± 0.7	0.0017 ± 16	0.008 ± 76	0.42 ± 0.02
24.6% act	1.4 ± 0.5	4.2 ± 1.0	0.076	0.0005 ± 0.0090	0.5 ± 1.0	5.9 ± 5.6	0.40 ± 0.03
31.7% act*	1.87 ± 0.07	1.9 ± 0.2	0	0.0001 ± 0.0026	0.003 ± 1.016	0.03 ± 11	0.48 ± 0.04
37.4% act*	0.88 ± 0.10	2.8 ± 0.1	0	0.0002 ± 0.0079	0.002 ± 0.192	0.04 ± 2.6	0.48 ± 0.05

Unless otherwise noted, electrodes were activated to 18% mass loss and were tested in 20 mM NaCl.

* The impedance data was fit using a modified equivalent circuit in which the wall capacitive component was replaced with a constant phase element such that Eqn. 4 becomes

$Z_w = \left(C_w (i\omega)^{n_2} + \frac{1}{R_{ct} + Z_s} \right)^{-1}$. $n_2 = 0.89, 0.90, 0.98, 2 \times 10^{-5}$ and 0.06 for the 2000 mM, 18% cell 1, 18% cell 2, 31.7%, and 37.4% samples respectively. For all other fits $n_2 = 1$ so Eqn. 4 holds as originally written.

Parameter Definitions

Below is a table of the parameters used in the main text and SI along with their corresponding definitions and typical units.

Table S2: Parameter Definitions

Parameter Symbol	Definition	Typical Unit
Z_{2w}	cell impedance as measured in a 2-wire mode	Ω or $\Omega\text{-cm}^2$
Z_{EEI}	external electronic impedance; includes external wires, contact between electrodes and current collectors, and current collector resistance	Ω or $\Omega\text{-cm}^2$
Z_{4w}	cell impedance excluding external wires and contacts as measured in a 4-wire mode	Ω or $\Omega\text{-cm}^2$
$R_{EER,s}$	series component of the external electronic impedance	Ω or $\Omega\text{-cm}^2$
$R_{contact}$	resistance of the contacts between the current collector and electrode	Ω or $\Omega\text{-cm}^2$
ω	angular frequency of applied voltage	rad/s
$C_{contact}$	capacitance of the contacts between electrodes and current collectors	F
R_{IER}	internal electronic resistance as measured in 4-wire mode, largely due to solid electrode resistance perpendicular to the applied electric field	Ω or $\Omega\text{-cm}^2$
R_{sp}	ionic resistance within the separator	Ω or $\Omega\text{-cm}^2$
R_{mA}	ionic resistance of macropores in the electrode	Ω or $\Omega\text{-cm}^2$
Z_w	macropore wall impedance	Ω or $\Omega\text{-cm}^2$
C_w	macropore wall capacitance	F
R_{ct}	internal ionic-transfer resistance*	Ω or $\Omega\text{-cm}^2$
Z_{st}	storage pore impedance	Ω or $\Omega\text{-cm}^2$
R_{st}	storage pore resistance	Ω or $\Omega\text{-cm}^2$
τ_{st}	storage pore characteristic time; $\tau_{st} = R_{st} C_{st}$	s
n	anomalous diffusion order parameter	—
R_{2w}	cell resistance as measured in a 2-wire setup; $R_{2w} = \max[\text{Re}(Z_{2w})]$	Ω or $\Omega\text{-cm}^2$
R_{4w}	cell resistance as measured in a 4-wire setup; $R_{4w} = \max[\text{Re}(Z_{4w})]$	Ω or $\Omega\text{-cm}^2$
R_{EER}	external electronic resistance $R_{EER} = \max[\text{Re}(Z_{EEI})] = R_{EER,s} + R_{contact} = R_{2w} - R_{4w}$	Ω or $\Omega\text{-cm}^2$
R_{el}	resistance of one electrode	Ω or $\Omega\text{-cm}^2$
l_{sp}	thickness of the separator	μm
τ_{sp}	separator tortuosity	—
A	electrode face area	cm^2
κ	electrolyte conductivity	mS/cm
p_{sp}	porosity of separator	—
l_{el}	electrode thickness	μm
τ_{mA}	electrode macropore tortuosity	—
p_{mA}	electrode macroporosity	—
σ	electrode conductivity; here $22 \pm 8 \text{ S/cm} = \sigma \gg \kappa$	S/cm
R_s	series resistance; defined as the high frequency intercept of the 2-wire impedance with the real axis	Ω or $\Omega\text{-cm}^2$

*Some work uses R_{ct} to refer to contact resistance but here R_{ct} is only used in reference to internal ionic-transfer resistance.¹

The parameters used here can be related to resistance terms commonly seen in the literature by the following equations.

$$R_s = R_{sp} + R_{IER} + R_{EER} \quad (\text{S1})$$

$$R_{EER} = R_{contact} + R_{EER,S} \quad (\text{S2})$$

Note that in the past, internal and external electronic resistances have been combined into one electronic resistance term; however this is impractical when comparing two- and four-wire measurements as is done here. Here, external electronic resistance is that due to wires, contacts, and current collectors and this resistance can be removed from measurements by using a 4-wire measurement mode. The internal electronic resistance remains even in 4-wire measurements and is due to features such as the solid electrode electronic resistance.

References

- (1) Qu, Y.; Baumann, T. F.; Santiago, J. G.; Stadermann, M. Characterization of Resistances of a Capacitive Deionization System. *Environ. Sci. Technol.* **2015**, *49*, 9699–9706.