Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology.
This journal is © The Royal Society of Chemistry 2022

Supplementary Information for

A comparison of strong-acid and weak-acid functionalized carbon electrodes in capacitive deionization

Rana Uwayid [a], Charles E. Diesendruck [b], Matthew E. Suss *[a,c,d]

[a] Faculty of Mechanical Engineering, Technion – Israel Institute of Technology, Haifa, Israel
[b] Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Haifa, Israel
[c]Wolfson Department of Chemical Engineering, Technion – Israel Institute of Technology, Haifa, Israel
[d] Grand Technion Energy Program, Technion – Israel Institute of Technology, Haifa, Israel

*Corresponding author, email: mesuss@technion.ac.il

1. Material characterizations

1.1 Nitrogen adsorption analysis

Table S1

Specific surface areas and micropore volumes of various electrodes both pre- and post-experiment, as calculated from N_2 sorption isotherms at 77 K.

Sample		**S_{BET} (m^2/g)**	**V_m (cm^3/g)**
Pristine pre-experiment		1855	0.68
Oxidized material pre-experiment		1500	0.52
Sulfonated pre-experiment		1447	0.55
SP Cell	Anode (Pristine)	1371	0.55
	Cathode (Sulfonated)	1508	0.56
OP Cell	Anode (Pristine)	1880	0.61
	Cathode (Oxidized)	1420	0.43

1.2 Fourier transform infrared spectroscopy

Transmission Fourier Transform Infrared (FTIR) spectra of the pre-experiment electrode materials.

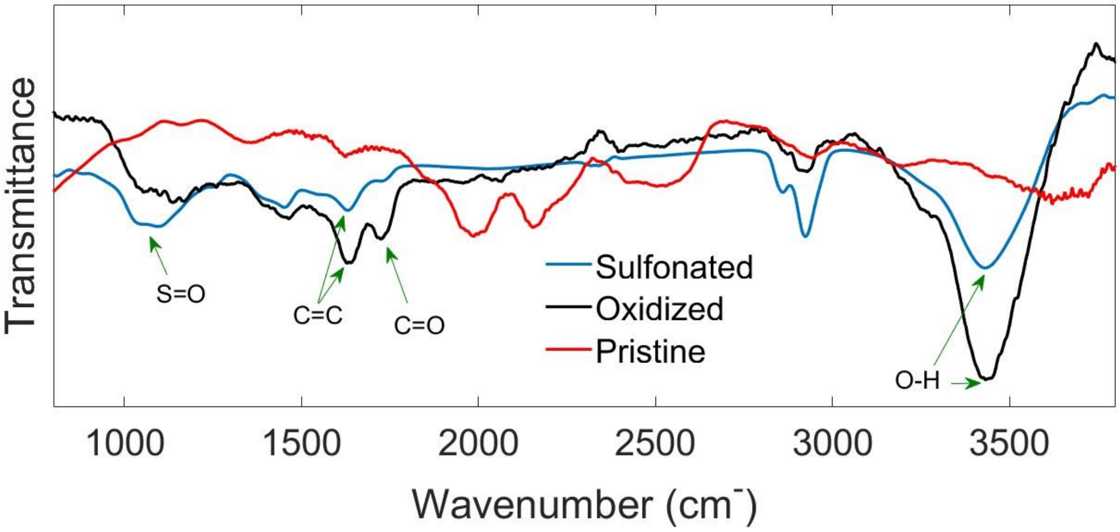

Figure S1. Measured transmission FTIR spectra for the pre-experiment pristine, oxidized, and sulfonated material

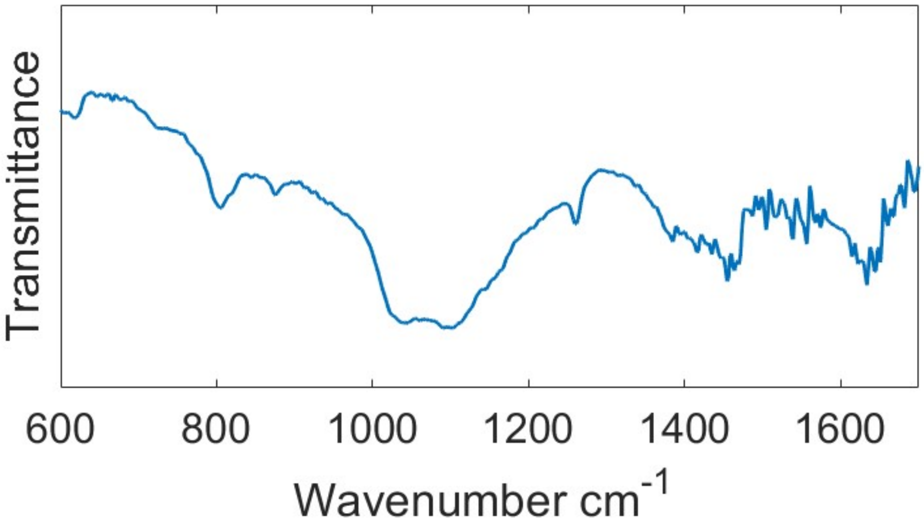

Figure S1.1. Zoom in measured transmission FTIR spectra for sulfonated material

1.3 Material morphology

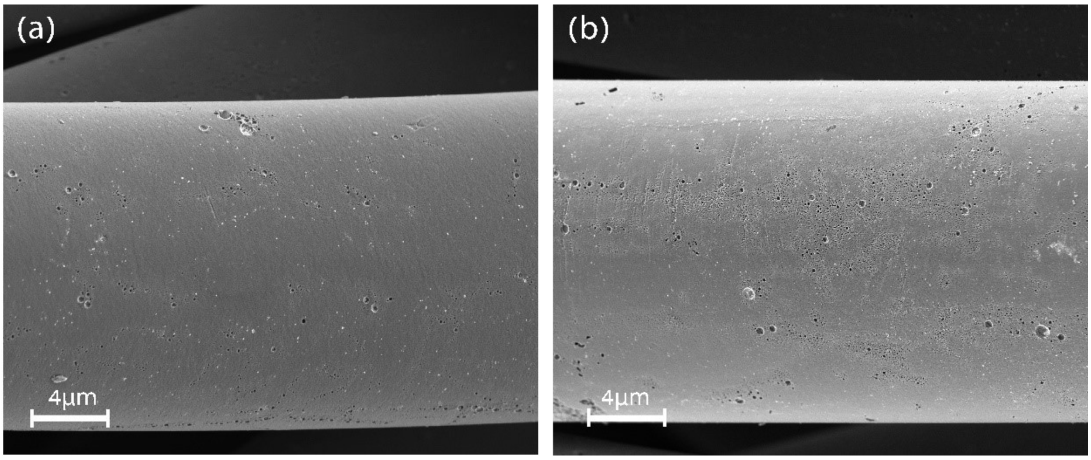

Figure S2. SEM images of (a) pristine and (b) sulfonated material pre-experiment.

2. Titration Model

A micropore EDL model[1,2] including a strong-acid term is used to extract micropore chemical charge concentrations. The model considers a weak acid group, A_1, a strong acid group A_2, and a weak base group, B, which dissociate according to,

$HA_1 \leftrightharpoons H^+ + A_1{}^-$

$BH^+ \leftrightharpoons B + H^+$

$HA_2 \rightarrow A_2 + H^+$

$C_{A,1}$ is defined as the total micropore weak-acid group concentration, including both the protonated, C_{AH}, and deprotonated form, C_{A^-}. Similarly, $C_{A,2}$ is defined as the total micropore strong-acid group concentration, which consists uniquely of the deprotonated sulfonic group form C_{SO3-}. As well, C_B is defined as the total micropore surface basic group concentration, including both the charged form, C_{BH+}, and uncharged form, C_B. The equilibrium constants are used as fitting parameters were K_{a1} for weak acid groups, defined as $K_{a1} = \frac{C_{m,H+} C_{A_1^-}}{C_{HA1}}$, and K_b for base groups, $K_b = \frac{C_{m,H+} C_B}{C_{BH^+}}$ where $C_{m,H+}$ is the micropore hydronium ion concentration. Since we assume that the weak acid group is mainly carboxylic acid, K_{a1} has been restricted to a range of 10^{-4} to 10^{-5}.

The model assumes an electrode with mass, m, immersed in a strong base solution containing sodium hydroxide, NaOH, of initial volume V_0 and concentration C_{NaOH}. At equilibrium, this solution is titrated with volume V of a strong acid, here hydrochloric acid, HCl. Two phases are considered, the electrode micropore phase and the bulk solution. The first equation is electroneutrality in the bulk,

$$(1)\ C_{Na^+} + C_{H^+} - C_{Cl^-} - C_{OH^-} = 0$$

Where C_{OH^-} is the hydroxide concentration that is replaced by $\frac{K_w}{C_{H^+}}$ in which K_w is the water disscociation constant, C_{H^+} is the hydroxyl concentration and can be written as 10^{-pH}, and C_{Na+} and C_{Cl^-} are the bulk concentration of sodium and chloride ions, respectively. No external electric potential is applied to the electrode. However, the presence of charge functional groups, and a non-zero net micropore chemical charge, σ_{chem}, results in a Donnan potential drop, $\Delta\phi_D$, to form between the micropores and the bulk which can electrosorb ions. Thus, the electrode charge balance is,

$$(2)\ \sigma_{ionic} + \sigma_{chem} = 0$$

The ions are assumed to be point charges, so the micropore ion concentrations are given by Boltzmann distributions leading to

$$(3)\ \sigma_{ionic} = -2(C_{Na+} + C_{H+}) sinh(\Delta\phi_D)$$

$$(4)\quad \sigma_{chem} = F\left(-\frac{C_{A^-}+C_{HA}}{1+C_{m,H^+}/K_{A1}} - \frac{C_{SO_3}}{1+C_{m,H^+}} + \frac{C_B+C_{BH^+}}{1+K_{A_3}/C_{m,H^+}}\right)$$

The final equations are the mass conservation of salt ions,

$$(5)\quad VC_{HCl} - mv_{mi}C_{Cl^-}\exp(\Delta\phi_D) - (V_0+V-mv_{mi})C_{Cl^-} = 0$$

$$(6)\quad V_0C_{NaOH} - mv_{mi}C_{Na^+}\exp(-\Delta\phi_D) - (V_0+V-mV_{mi})C_{Na^+} = 0$$

Where v_{mi} is the micropore volume.

Equations (1) – (6) are solved simultaneously and fitted to the experimental data.

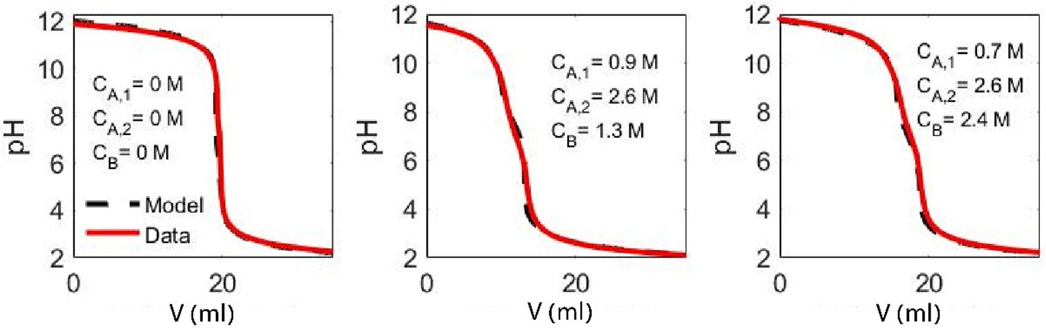

Figure S3. Results of model-to-data fitting, showing experimental titration data (red solid lines) and micropore EDL theory results (black dashed lines) (a) Blank titration without any carbon material, (b) sulfonated material pre-experiment, (c) sulfonated material post-experiment

Figure S3 shows the experimental titration data and the model-to-data-fitting for the sulfonated material pre- and post-experiment. Model-to data-fitting for the pre-experiment material yields best-fit $C_{A,1}$ = 0.9 M $C_{A,2}$=2.6 M and C_B = 1.3 M (Figure S3b). Slight deviation between the data and model can be seen, for example, in the area around pH = 7-9 which corresponds to the weak base pKa. We hypothesize such deviations are due to our use of a single value for basic group pKa, where in reality there may be several groups with differing pKas. The sulfonated material post-experiment shows higher basic group concentrations of C_B = 2.6 M, indicating that CDI operation added a large amount of base groups to micropores. There was no significant change in strong acid concentration during CDI cycling indicating that sulfonic groups are quite stable.

References

1 E. N. Guyes, T. Malka and M. E. Suss, *Environ. Sci. Technol.*, 2019, **53**, 8447–8454.

2 A. Hemmatifar, D. I. Oyarzun, J. W. Palko, S. A. Hawks, M. Stadermann and J. G. Santiago, *Water Res.*, 2017, **122**, 387–397.