

Supplementary Information for:

On the Dynamics of Charging in Nanoporous Carbon-Based Supercapacitors

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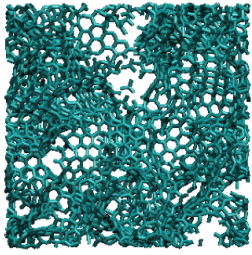
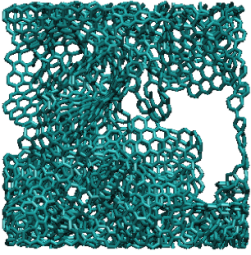
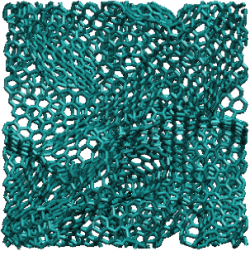
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Computational details

Table 1: Number of carbon atoms and lengths of the simulation cell in the z direction. The lengths in the x and y directions were the same (two dimensional periodic boundary conditions are used, i.e. there is no periodicity in the z direction).

Type of carbon	CDC-800	CDC-950	CDC-1200
Snapshots			
Number of carbon atoms	3821	3276	3649
$L_x = L_y$ (nm)	4.33	4.36	4.37
L_z (nm)	18.55	18.64	18.64

Variation of temperature due to Joule effect

Upon application of a constant potential difference, the increase in temperature due to the Joule effect is associated with the creation of an electric current across the cell and follows Ohm's law.¹ Figures 1, 2 and 3 show this increase of temperature.

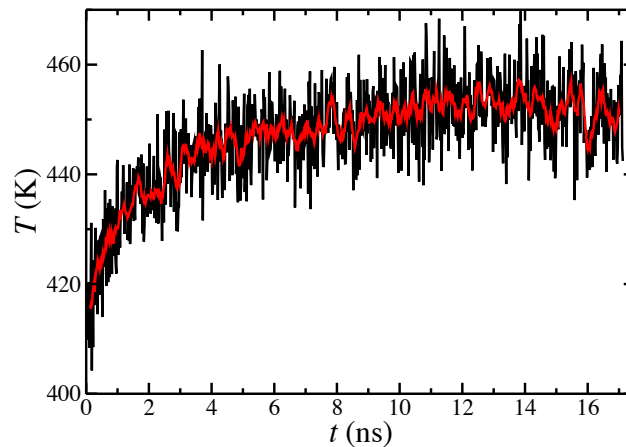


Figure 1: Variation of temperature with time for CDC-800. Black: raw data, red: running average (over 10 points).

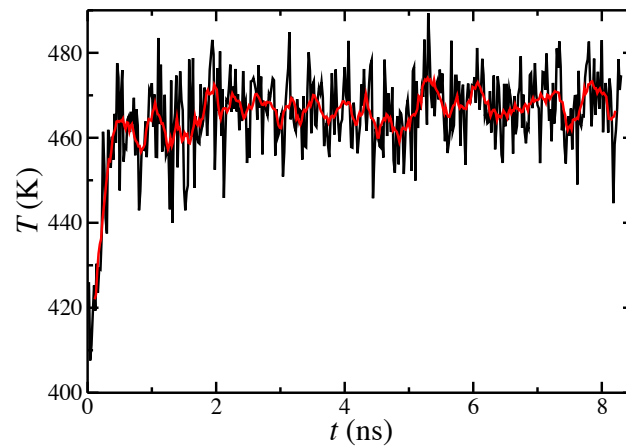


Figure 2: Variation of temperature with time for CDC-950. Black: raw data, red: running average (over 10 points).

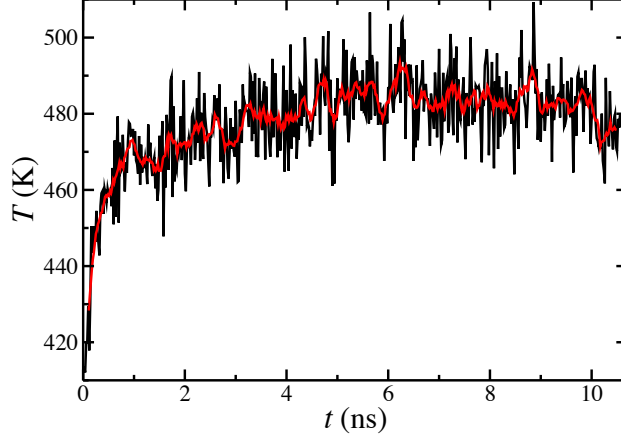


Figure 3: Variation of temperature with time for CDC-1200. Black: raw data, red: running average (over 10 points).

Equivalent circuit

Here we present the analytical results for the charging of the equivalent circuit described in Figure 1 of the manuscript, which are used to analyze the molecular simulation data. From the impedance associated with each component, namely R_{bulk} , R_l , $1/jC_1\omega$ and $1/jC_2\omega$, and their combination in series and in parallel, the overall impedance of the simulation cell is easily derived as:

$$Z(\omega) = \frac{(j\omega)^2 R_l (R_{bulk} + 2R_l) C_1 C_2 + j\omega [(R_{bulk} + 2R_l) C_1 + (R_{bulk} + 4R_l) C_2] + 2}{(j\omega)^2 R_l C_1 C_2 + j\omega (C_1 + C_2)} \quad (1)$$

In Fourier space, the total charge Q of the electrodes is related to the voltage V as:

$$Q(\omega) = \frac{I(\omega)}{j\omega} = \frac{V(\omega)}{j\omega Z(\omega)}, \quad (2)$$

where we have used the definition of the impedance and the fact that the intensity I is the time derivative of the charge. From equation 1, it then follows that:

$$[(j\omega)^2 + j\omega a + b] Q(\omega) = [c + j\omega d] V(\omega), \quad (3)$$

with

$$\begin{aligned}
a &= \frac{(R_{bulk} + 2R_l)C_1 + (R_{bulk} + 4R_l)C_2}{R_l(R_{bulk} + 2R_l)C_1C_2} \\
b &= \frac{2}{R_l(R_{bulk} + 2R_l)C_1C_2} \\
c &= \frac{C_1 + C_2}{R_l(R_{bulk} + 2R_l)C_1C_2} \\
d &= \frac{1}{R_{bulk} + 2R_l} .
\end{aligned}$$

Consequently, the total charge $Q(t)$ satisfies the following differential equation:

$$Q''(t) + aQ'(t) + bQ(t) = cV(t) + dV'(t) , \quad (4)$$

with the same coefficients a , b , c and d . This linear differential equation is then solved for the choice of potential corresponding to a jump from 0 to $V_0 = 1$ V at $t = 0$, i.e. $V(t) = V_0\Theta(t)$, with Θ the Heaviside function - hence $V'(t) = V_0\delta(t)$, with δ the Dirac distribution. In particular, at $t = 0^-$ the charge Q and intensity Q' both vanish. The solution reads, for $t > 0$:

$$Q(t) = Q_{max} \left[1 - A_1 \exp\left(-\frac{t}{\tau_1}\right) - A_2 \exp\left(-\frac{t}{\tau_2}\right) \right] , \quad (5)$$

as indicated in the manuscript, with the following expressions for the constants:

$$\begin{aligned}
Q_{max} &= \frac{c}{b}V_0 = \frac{C_1 + C_2}{2}V_0 \\
\tau_1 &= \frac{2}{a + \sqrt{a^2 - 4b}} \\
\tau_2 &= \frac{2}{a - \sqrt{a^2 - 4b}} \\
A_1 &= \frac{1}{2} \left[1 + \frac{2bd - ac}{2c\sqrt{a^2 - 4b}} \right] \\
A_2 &= \frac{1}{2} \left[1 - \frac{2bd - ac}{2c\sqrt{a^2 - 4b}} \right] .
\end{aligned}$$

The charges Q_1 and Q_2 of both slices of the electrode can also be determined from the impedance of each branch of the circuit. One finds for example that Q_1 satisfies the same equation 4 as the total charge, with the same values of the coefficients a and b , but with c and d replaced by $c_1 = 1/R_l(R_{bulk} + 2R_l)C_1$ and d_1 . The solution for $Q_1(t)$ is then obtained by replacing these coefficients in the solution for $Q(t)$. The charge of the second slice then immediately follows as $Q_2(t) = Q(t) - Q_1(t)$.

Among all the parameters introduced in this model, only R_l is unknown. Indeed, R_{bulk} can be deduced from the electrical conductivity σ . For the latter, we have to take into account the temperature increase observed during the first nanoseconds of simulation. Values of 4.5, 5.0 and 5.3 S m⁻¹ were respectively taken for CDC-800, CDC-950 and CDC-1200 following the simulation data of Roy and Maroncelli² (note that taking the average value, i.e. 5.0 S m⁻¹ for all the CDCs would only change the final R_l very slightly). C_1 and C_2 are given by the final total charge in the two slices of the electrodes. We have fitted R_l on $Q(t)$ using a least-square method; and the corresponding results are provided in the Table 1 of the manuscript.

Charging dynamics for an applied potential of 2 V

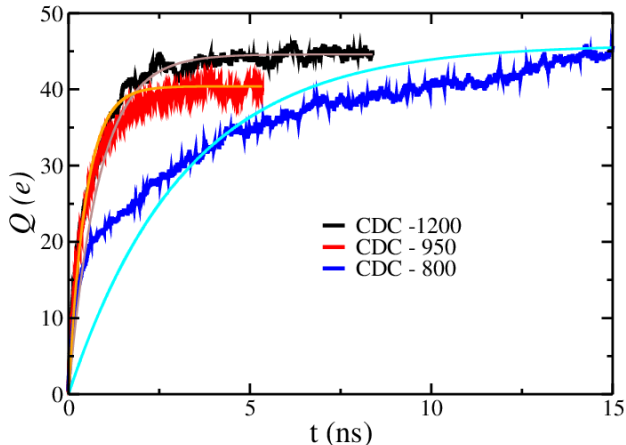


Figure 4: Total charge of the electrodes as a function of time for an applied potential of 2 V. The simulation results are compared with those obtained using equation 5, with the R_l parameter extracted from the simulations at 1 V (maroon: CDC-1200, orange: CDC-950, cyan: CDC-800).

In order to illustrate the transferability of the R_l parameter fitted from our simulations with an applied potential of 1 V to other conditions, we compare on figure 4 the total charge predicted using this parameter (with no further fitting) with the simulation results for an applied potential of 2 V. A good agreement is obtained.

References

- (1) Merlet, C.; Péan, C.; Rotenberg, B.; Madden, P. A.; Simon, P.; Salanne, M. Simulating Supercapacitors: Can We Model Electrodes As Constant Charge Surfaces? *J. Phys. Chem. Lett.* **2013**, *4*, 264–268.
- (2) Roy, D.; Maroncelli, M. An Improved Four-Site Ionic Liquid Model. *J. Phys. Chem. B* **2010**, *114*, 12629–12631.