A blessing and a curse: how a supercapacitor’s large capacitance causes its slow charging

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The development of novel electrolytes and electrodes for supercapacitors is hindered by a gap of several orders of magnitude between experimentally measured and theoretically predicted charging time scales. Here, we propose an electrode model, containing many parallel stacked electrodes, that explains the slow charging dynamics of supercapacitors. At low applied potentials, the charging behavior of this model is described well by an equivalent circuit model. Conversely, at high potentials, charging dynamics slow down and evolve on two relaxation time scales: a generalized $RC$ time and a diffusion time, which, interestingly, become similar for porous electrodes. The charging behavior of the stack-electrode model presented here helps to understand the charging dynamics of porous electrodes and agrees qualitatively with experimental time scales measured with porous electrodes.

In the electric energy storage domain, supercapacitors [Fig. 1(a)] have proven their value in applications requiring higher power output than delivered by batteries and more energy than stored in dielectric capacitors [1–4]. Many types of carbon-based materials have been used for the capacitor’s electrodes [5–7]. However, the relation between the porous structures and the charging dynamics of macroscopic supercapacitors is poorly understood. On the one hand, transmission line (TL) models [8–11] can successfully fit experimental data, but the fit parameters therein do not have a direct interpretation in terms of microscopic properties of supercapacitors. On the other hand, molecular dynamics simulation [12–17], lattice Boltzmann simulations [18, 19], and classical dynamic density functional theory [20–22] can elucidate the charging mechanisms of a single or a few nanopores or a nanoscale anode-cathode model, but predicted relaxation time scales are of the order of ns, roughly 12 orders of magnitude smaller than experimentally measured $10^3$ s timescales of supercapacitors [23–26]. To describe the charging of supercapacitors, one needs to account for both the ionic currents from the ion reservoir that separates the anode and cathode through a macropore network into the nanopores (micrometers) and for the electric double layer (EDL) buildup therein (nanometers). Clearly, such a multi-scale analysis cannot be performed with the above mentioned simulation techniques alone, as computational power limits simulations to nanoscale systems. In this Letter, we present a minimal model to explain the long experimental relaxation timescales of supercapacitors instead.

The canonical model describing ionic charge relaxation to an applied electric field employs a dilute 1:1 electrolyte and two parallel and planar blocking electrodes separated by a distance $2L$ [27]. Suddenly applying a potential difference $2\Psi$ with a battery, the two electrodes will acquire opposite surface charge densities $\pm e\sigma(t)$, screened in the electrolyte by two EDLs, whose

\[ i = 1 \quad i = n \]

\[ 2\Psi \]

\[ 2L \quad H \]

\[ \rho_0 \]

\[ -\Psi \]

\[ h \]

\[ \Psi \]

\[ 2L \quad H \]

\[ C \quad 2C \quad 2\Psi \]

\[ 1 \quad 2 \quad n \]

\[ R' \quad R' \quad R \]

\[ 1 \quad 2 \quad n \]

\[ \rho_0 \]

\[ \Psi \]

\[ 2L \quad H \]

\[ C \quad 2C \quad 2\Psi \]

\[ 1 \quad 2 \quad n \]

\[ R' \quad R' \quad R \]

\[ 1 \quad 2 \quad n \]

\[ \rho_0 \]

\[ \Psi \]

\[ 2L \quad H \]

\[ C \quad 2C \quad 2\Psi \]

\[ 1 \quad 2 \quad n \]

\[ R' \quad R' \quad R \]

\[ 1 \quad 2 \quad n \]

\[ \rho_0 \]

\[ \Psi \]

\[ 2L \quad H \]

\[ C \quad 2C \quad 2\Psi \]

\[ 1 \quad 2 \quad n \]

\[ R' \quad R' \quad R \]

\[ 1 \quad 2 \quad n \]

\[ \rho_0 \]

\[ \Psi \]

\[ 2L \quad H \]

\[ C \quad 2C \quad 2\Psi \]

\[ 1 \quad 2 \quad n \]

\[ R' \quad R' \quad R \]

\[ 1 \quad 2 \quad n \]

\[ \rho_0 \]

\[ \Psi \]

\[ 2L \quad H \]

\[ C \quad 2C \quad 2\Psi \]

\[ 1 \quad 2 \quad n \]

\[ R' \quad R' \quad R \]

\[ 1 \quad 2 \quad n \]

\[ \rho_0 \]

\[ \Psi \]
equilibrium width is characterized by the Debye length \( \kappa^{-1} = \sqrt{\varepsilon k_B T/2e^2 \rho_b} \), with \( 2 \rho_b \) the bulk ion number density, \( \varepsilon \) the electrolyte permittivity, \( e \) the elementary charge, and \( k_B T \) the thermal energy. At late times and for \( \kappa L \gg 1 \), \( \sigma(t) = 2 \Phi \rho_b \kappa^{-1} [1 - \exp(-t/\tau_{RC})] \), with \( 2 \Phi = 2 e \Psi/k_B T \) the dimensionless applied potential, \( \tau_{RC} = \kappa^{-1} L/D \) the dimensionless applied potential, \( \tau_{RC} = \kappa^{-1} L/D \) the dimensionless applied potential, and \( D \) the ionic diffusion coefficient [27–29]. Inserting typical experimental parameters \( \kappa^{-1} \approx 1 \) nm, \( L \approx 250 \mu m \), and \( D \approx 1 \times 10^{-9} \text{m}^2 \text{s}^{-1} \) yields \( \tau_{RC} \approx 10^{-4} \text{s} \); larger than the timescales predicted by molecular simulations, but still five orders of magnitude smaller than the experimental charging time of supercapacitors. This discrepancy comes as no surprise as the above \( \sigma(t) \) applies to planar electrodes: this model does not account for the huge surface area and for the ion transport through the porous structure of the supercapacitor electrodes. Simple extensions of the flat electrode setup were discussed, such as spherical and cylindrical electrodes [19, 30] and a single cylindrical pore in contact with a reservoir [9]. Several theoretical works focused on the charging dynamics of porous electrodes [31, 37]. Still, the gap between experimental and theoretical supercapacitor charging timescales has not been bridged yet.

To explain why the charging time of macroscopic porous electrodes [Fig. 1(a)] is much larger than that of flat electrodes, in this Letter, we will characterize the charging dynamics of the model shown in Fig. 1(b) and also compare it to the charging dynamics of the circuit shown in Fig. 1(c). In our model, the nanoporous cathode and anode of a supercapacitor are both modeled by a stack of \( n \) parallel electrodes with an equal spacing \( h \) mimicking the pore size, such that the thickness of the cathode and anode equals \( H = (n-1)h \). The surface area \( A \) of all individual electrodes is assumed to be sufficiently large that we can ignore edge effects and study all macroscopic observables as a function of a single coordinate \( x \) perpendicular to the electrode surfaces. We adopt a coordinate system whose origin lies in the middle \((x = 0)\) of the system and where the \( i \)th cathode and anode, with \( i = 1, \ldots, n \), are located at \( X_i = \pm [L + (i-1)h] \). All parallel stacked electrodes are fully permeable to the electrolyte in order to mimic the porosity of supercapacitor electrodes, except the two outer ones \((i = n)\) which are impermeable to have a closed system [cf. Eq. 25]. The ionic number densities \( \rho_{\pm}(x, t) \) and ionic fluxes \( j_{\pm}(x, t) \) are thus continuous at each \( X_i \). Initially, the ionic number densities are homogenous

\[
\rho_{\pm}(x, t = 0) = \rho_b, \quad |x| \leq L + H. \tag{1}
\]

At time \( t = 0 \), a dimensionless potential difference \( 2 \Phi \) is applied to the macroscopic cathode and anode. This yields the following boundary conditions for \( t > 0 \),

\[
\phi(\pm X_i, t) = \pm \Phi; \quad j_{\pm}(\pm X_i, t) = 0, \tag{2a}
\]

with \( \phi(x, t) \) the electric potential in units of the thermal voltage \( k_B T/e \). To model the ionic dynamics, we use the classical Poisson-Nernst-Planck (PNP) equations [27]

\[
\frac{\partial^2 \phi(x, t)}{\partial x^2} = -\kappa^2 \left[ \frac{\rho_r(x, t) - \rho_b(x, t)}{2 \rho_b} \right]; \tag{3a}
\]

\[
\partial_t \rho_{\pm}(x, t) = -\partial_x j_{\pm}(x, t); \tag{3b}
\]

\[
j_{\pm}(x, t) = -D \left[ \partial_x \rho_{\pm}(x, t) \pm \rho_{\pm}(x, t) \partial_x \phi(x, t) \right]. \tag{3c}
\]

In Eqs. 1, 2, and 3 appear the applied potential \( \Phi \) and 4 length scales: \( h, H, L, \) and \( \kappa^{-1} \). With these parameters, we can construct many different combinations that yield 1-3 independent dimensionless parameters, for instance: \( \Phi, \kappa L, \kappa H, \) and \( \kappa h \) or, equivalently, \( \Phi, \kappa L, H/L, \) and \( n \). We focus here on the latter choice and mostly restrict to \( H/L = 1 \), which is reasonable for supercapacitors.

In Fig. 2(a), we present numerical results for \( \phi(x, t) \) for a low potential \( \Phi = 0.001 \) and \( \kappa L = 100, H/L = 1, \) and \( n = 5 \). These parameters correspond to \( \kappa h = 25 \), which means that the EDLs are thin compared to the electrode separations. Initially, the potential in the reservoir \(|x| < L\) displays a typical linear \( x \) dependence, which corresponds to a spatially constant electric field. At later times, the potential retains this linear dependence in the reservoir, albeit with a slope that decreases with time due to the build-up of EDLs. At short times \( t/\tau_{RC} \leq 2 \), there is a clear asymmetry between the two EDLs that surround individual planar electrodes. This asymmetry is lost at later times \( t \geq 20 \tau_{RC} \), when the EDLs fully equilibrate.

For the same parameters, in Fig. 2(b) we show the surface charge densities \( \sigma_i \) of the individual electrodes (labeled with \( i \)), which we find with Gauss’ law \( \sigma_i(t) = -2 \rho_b \kappa^{-1} [\partial_x \phi|_{X_i^+} - \partial_x \phi|_{X_i^-}] \). At early times \( t < \tau_{RC} \), the electrodes charge faster the closer they are situated to the reservoir, \( \sigma_1 > \sigma_2 > \ldots > \sigma_n \). However, the late-time relaxation timescale is the same for all electrodes: all electrodes reach 99.9% of their equilibrium charge around \( t/\tau_{RC} \approx 50 \). As the outer electrodes face the electrolyte only at one side, we have \( \partial_x \phi|_{X_n^+} = \partial_x \phi|_{-X_n^-} = 0 \), and \( \sigma_i(t/\tau_{RC} \to \infty) \) is a factor two smaller than the other electrodes. To better understand these phenomen-
In order to study the behavior of the circuit model, we derived predictions for the time-dependent charge on each capacitor in this circuit, which translates into a prediction for $\sigma(t)$ in the corresponding microscopic model, shown in Fig. 2(b) with symbols. Clearly, the predictions from the microscopic and circuit model are indistinguishable. In line with our earlier observation, the equivalent-circuit model predicts that all electrodes relax exponentially at late times with the same time constant $\tau_n$ given by

$$\frac{\tau_n}{\tau_{RC}} = \left(2 + 0.75 \frac{H}{L}\right) n - 1 - 0.91 \frac{H}{L},$$

which correctly reduces to $\tau_n = \tau_{RC}$ for $n = 1$ (for which $H/L = 0$). The coefficients 2 and 1 appearing here are analytical results obtained in the limit $H/L \to 0$. The other numerical factors in Eq. (4) are related to the smallest eigenvalue of an almost-Toeplitz matrix [cf. Eq. AII] that relates $n$ potential drops over the capacitors to $n$ (coupled) currents through the resistors. From Eq. (4) we see that $\tau_n$ is large whenever $n$ is large. This suggests that the large relaxation time of supercapacitors stems from their large internal surface area, achieved through many small pores.

Because supercapacitors are typically subjected to large potentials in practical applications, we also characterize the dynamics of the stack-electrode model at $\Phi > 1$. In Fig. 3(a), (c), and (e) we present data for $\Phi = \{0.01, 0.1, 1, 2\}$, $\kappa L = 100$, and $n = 1$ (hence $H/L = 0$). For this two-electrode setup, it is known that, next to $\tau_{RC}$, the diffusion time $L^2/D$ emerges in the ionic relaxation due to slow salt diffusion from the cell center to the electrode surfaces. Indeed, Fig. 3(a) shows that the normalized surface density $\sigma_n(t)/\sigma_{eq}$ with $\sigma_{eq} \equiv \sigma_n(t/\tau_{RC} \to \infty)$ the late-time surface charge density, develops slower at higher $\Phi$. Next, Fig. 3(c) shows the cell-center salt concentration $c(t) = [\rho_+(0,t) + \rho_-(0,t)]/(2\rho_b)$ for the same $\Phi$. We see that $c(t) \approx 1$ for $\Phi \leq 0.1$ and that $c(t)$ decreases at late times ($t/\tau_{RC} > 10$) by 0.1-1% for $\Phi = 1$ and 2: As our setup is closed, a net ionic adsorption on the electrodes “desalinates” the cell center. To investigate the emergence of the slow timescale at large applied potentials, in Fig. 3(e) we show the charge relaxation $1 - \sigma(t)/\sigma_{eq}$ (solid lines) and the concentration decay $(c(t) - c_{eq})/(1 - c_{eq})$ (dashed lines), where $c_{eq} \equiv c(t/\tau_{RC} \to \infty)$. At early times ($t/\tau_{RC} < 1$), all data for $1 - \sigma(t)/\sigma_{eq}$ collapse onto the $\Phi = 0.01$ curve, indicating that the initial ionic relaxation is described well by the equivalent circuit model, even for higher $\Phi$. Thereafter, a second, slower relaxation emerges in $1 - \sigma(t)/\sigma_{eq}$, emerging more dominantly for higher $\Phi$. At late times, the slopes of $1 - \sigma(t)/\sigma_{eq}$ and $(c(t) - c_{eq})/(1 - c_{eq})$ are the same. Numerical results [cf. Fig. B2(d)] for the adsorption timescale $\tau_{ad}$, the inverse of these slopes, show that $\tau_{ad}/\tau_{RC}$ is independent of $\Phi$ (for all $\Phi$ considered) and scales linearly with $\kappa L$. Using the definition of $\tau_{RC}$, we then recover the $L^2/D$-scaling of $\tau_{ad}$ suggested by Ref. 27.

To investigate the effect of $n > 1$ for high potentials, in Fig. 3(b), (d), and (f) we plot the same observables as in Fig. 3(a), (c), and (e), now for $\Phi = 2$, $\kappa L = 100$, $H/L = 1$, and $n = \{2, 3, 6\}$. Similar to our $\Phi = 0.001$-findings [condensed in $\tau_n$ of Eq. (4)], we see that the charging dynamics at $\Phi = 2$ also slows down with increasing $n$. The cell-center salt concentration $c(t)$ [Fig. 3(d)] is again unaffected at early times $t/\tau_{RC} < 5$, after which it decays to an equilibrium value that decreases with $n$. Our model thus recovers the intuition that for two electrodes of the same volume, the one with more pores (and hence a large surface area) desalinates an electrolyte reservoir more. In Fig. 3(f) we see that the surface charge again
decays on two distinct timescales. Plotting the same data with time scaled by $\tau_n$ instead of by $\tau_{RC}$ [cf. Fig. 3(c)], all $1 - \sigma(t)/\sigma_{eq}$ collapse for $t \leq \tau_n$, which shows that the circuit model decently describes the early-time relaxation at high potentials as well. Conversely, at late times, we see in Fig. 3(f) that $1 - \sigma(t)/\sigma_{eq}$ and $(c(t) - c_{eq})/(c_{eq})$ decay exponentially with a time constant $\tau_{ad}$ that does not depend on $n$ for the parameter set under consideration. Considering a larger set of $\kappa L$, $\kappa h$, and $n$, we show $\tau_{ad}$ in Fig. 4(a). From this figure we conclude that

$$\tau_{ad} = \alpha \frac{(H + L)^2}{D}$$

(5)

hence, the adsorption time $\tau_{ad}$ depends on the total system size. We show the $\kappa h$-dependent prefactor $\alpha$ in Fig. 4(b) for various $\kappa L$, which reveals that $\alpha$ is $\kappa L$ independent and that $\alpha \approx 0.1$ for $\kappa h > 10$, while $\alpha$ increases with decreasing $\kappa h < 10$.

Since $\tau_n$ [Eq. (3)] and $\tau_{ad}$ [Eq. (5)] depend on $\kappa L$, $\kappa h$, and $n$ differently, both $\tau_{ad}/\tau_n < 1$, $\tau_{ad}/\tau_n \approx 1$, and $\tau_{ad}/\tau_n \gg 1$ are possible. Focussing here on $n \gg 1$, which is relevant to macroscopic electrodes, we find

$$\frac{\tau_n}{\tau_{ad}} \approx \begin{cases} 
0.75 \frac{H}{\alpha k L} & L \gg H; \\
0.69 \frac{H}{\alpha k L} & L = H; \\
2 \frac{H}{\alpha k L} & L \ll H.
\end{cases}$$

(6)

For $H/L = 1$ (and $n \gg 1$) we find that $\tau_n/\tau_{ad} \sim 1$ whenever $\kappa h < 10$.

Finally, it is interesting to determine the applicability of our stack-electrode model to experiments. We consider here the setup of Ref. 24, where two carbon electrodes of thickness $H = 0.5$ mm, separation $2L = 2.2$ mm, porosity $p = 0.65$, mass density $\sigma = 5.8 \times 10^5$ g m$^{-3}$, and Brunauer-Emmett-Teller-area $A_{BET} = 1330$ m$^2$ g$^{-1}$ were used. Assuming each porous electrode to consist of two flat solid carbon slabs, we get a crude estimate for the pore size with $h = p/(\sigma A_{BET}) = 0.84$ nm. The electrodes were immersed in a 1 M NaCl solution at room temperature, hence, $\kappa^{-1} = 0.3$ nm and bulk diffusivity $D = 1.6 \times 10^{-9}$ m$^2$s$^{-1}$. [We ignore that $D$ is smaller in nanopores 21 39 and that different diffusivities may appear in Eqs. 4 and 5 42.] These parameters correspond in our model to $H/L = 0.45$, $n = 5.9 \times 10^6$, and $\kappa h = 2.8$ hence $\alpha = 0.3$. With Eqs. 4 and 5 we now find $\tau_n = 2.9 \times 10^4$ s and $\tau_{ad} = 4.8 \times 10^2$ s, roughly within one order of magnitude from the two timescales $(2 \times 10^2$ s and $9 \times 10^3$ s) observed in the experimental data of Ref. 25 (see Appendix C). Given the simplicity of our model and crudeness of our estimates of $\kappa h$, $n$, and $D$, the remaining discrepancies are not surprising. Yet, the stack-electrode model has bridged the five-orders-of-magnitude gap between experimental relaxation times and those predicted in the $n = 1$ model.

In summary, we studied the charging dynamics of nanoporous electrodes with a simple electrode model. At small applied potentials, numerical simulations of the PNP equations are reproduced accurately by an equivalent circuit model. This circuit model is akin to TL models used often to fit experimental supercapacitor data. Notably, however, the resistances, capacitances, and number of branches in the circuit model are not fit parameters but physically determined by our microscopic model. This one-to-one relation allows us to interpret the long relaxation time of supercapacitors as being due to large number of pores $n$ in nanoporous electrodes: The stack-electrode model relaxes with the timescale $\tau_n \sim (2 + 0.75H/L)n\tau_{RC}$. At higher potentials, the surface charge relaxes at early times with $\tau_n$. Higher potentials, however, lead to slow salt adsorption in the EDLs and concomitant depletion of the reservoir on the timescale $\tau_{ad} \sim (L + H)^2/D$. As salt and charge transport are coupled, the long timescale $\tau_{ad}$ also governs the late-time surface charge relaxation, all the more so the higher the applied potential. The two time scales $\tau_n$ and $\tau_{ad}$ differ orders of magnitude for small $n$ but become similar when electrodes have many pores, as is the case for supercapacitors. Inserting parameters relating to a recent experimental study 24, our simple model predicts the two observed relaxation times roughly within one order of magnitude. Our model thus successfully bridged the five-orders-of-magnitude gap between theoretically predicted and experimentally measured timescales, and could serve as a basis for extensions that break the planar symmetry. However, more work is needed to fully understand the charging dynamics of porous capacitors, which should include effects due to finite ion sizes, more realistic modeling of pore morphology, Faradaic reactions, position-dependent diffusion coefficients, etc.
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Appendix A: Equivalent circuit model

We discuss an equivalent circuit model that describes the charging dynamics of the stack-electrode model well. Before turning to the general \( n \) case, we first discuss the easier \( n = 1 \) and \( n = 2 \) cases (see also Ref. [38]).

1. The case \( n = 1 \)

The trivial \( n = 1 \) case can be described by the circuit model shown in Fig. A1. The electric double layers (EDLs) on each electrode are modeled with a capacitor of capacitance \( C \). The electrolyte resistance is modeled through a resistor of resistance \( R \). At \( t = 0 \) a voltage source is switched on to provide a potential difference of \( 2\Psi \). The capacitors, initially uncharged, will acquire a charge \( Q(t) = C\Delta \Psi(t) \) with \( \Delta \Psi(t) \) being the time-dependent voltage difference between either sides of the capacitors. The current that flows through the system is found via Ohm’s law, \( I_R = [\Psi - \Delta \Psi(t)] - [\Psi + \Delta \Psi(t)] = 2[\Psi - \Delta \Psi(t)] \). With \( I = Q(t) = C\Delta \Psi(t) \), we find

\[
\Delta \Psi(t) = \frac{\Psi - \Delta \Psi(t)}{R} \frac{2}{RC}, \quad (A1a)
\]

\[
\Delta \Psi(t = 0) = 0, \quad (A1b)
\]

which is solved by

\[
\Delta \Psi(t) = \Psi \left[ 1 - \exp \left( -\frac{2t}{RC} \right) \right]. \quad (A2)
\]

To relate this result to the relaxation of EDLs that we are trying to mimic, note that the EDL capacitance and electrolyte resistivity read \( C = \Lambda \epsilon \kappa \) and \( R = 2L/(\Lambda \epsilon \kappa^2 D) \), respectively; hence, \( RC = 2\tau_{RC} = 2\kappa^{-1}L/D \).

2. The case \( n = 2 \)

For \( n = 2 \), we need to account for the fact that the inner electrode \( (i = 1) \) is facing the electrolyte twice, while the outer electrode \( (i = 2) \) faces it only once: we use \( 2C \) and \( C \) for the different capacitors, respectively, see Fig. A2. For this circuit, the charge on each of the capacitors (index increasing outwards) is \( Q_1(t) = 2C\Delta \Psi_1(t) \) and \( Q_2(t) = C\Delta \Psi_2(t) \). Meanwhile, for the currents \( I, I_1, \) and \( I_2 \) we have \( I = I_1 + I_2 \) (Kirchoff’s law), and \( IR = 2[\Psi - \Delta \Psi_1(t)] \) and \( I_R = 2[\Psi - \Delta \Psi_2(t)] \) (Ohm’s law). Combining the above equations gives two coupled differential equations

\[
\Delta \Psi_1(t) = \frac{I_1}{2C} = \frac{\Psi}{RC} - \left( \frac{1}{RC} + \frac{1}{2R'C} \right) \Delta \Psi_1(t) + \frac{1}{2R'C} \Delta \Psi_2(t), \quad (A3a)
\]

\[
\Delta \Psi_2(t) = \frac{I_2}{C} = \frac{1}{RC} \Delta \Psi_1(t) - \frac{1}{RC} \Delta \Psi_2(t), \quad (A3b)
\]

\[
\Delta \Psi_1(t = 0) = 0, \quad (A3c)
\]

\[
\Delta \Psi_2(t = 0) = 0. \quad (A3d)
\]

In matrix form this reads

\[
\begin{pmatrix}
\Delta \Psi_1(t) \\
\Delta \Psi_2(t)
\end{pmatrix} = \begin{pmatrix}
\frac{1}{2R'C} & 1 \\
-2 & \frac{1}{RC}
\end{pmatrix} \begin{pmatrix}
\Delta \Psi_1(t) \\
\Delta \Psi_2(t)
\end{pmatrix} + \begin{pmatrix}
\Psi \\
0
\end{pmatrix}, \quad (A4)
\]

which can be written as \( \dot{X} = Y - MX \), with

\[
X \equiv \begin{pmatrix}
\Delta \Psi_1(t) \\
\Delta \Psi_2(t)
\end{pmatrix}, \quad Y \equiv \begin{pmatrix}
\Psi \\
0
\end{pmatrix}, \quad \lambda \equiv \begin{pmatrix}
\lambda_+ & 0 \\
0 & \lambda_-
\end{pmatrix}
\]

\[
M = \frac{1}{2R'C} \begin{pmatrix}
1 + 2R'/R & -1 \\
-2 & \frac{1}{RC}
\end{pmatrix} = UDU^{-1}, \quad (A5)
\]

with \( UU^{-1} = U^{-1}U = 1 \) and \( D = \frac{1}{2R'C} \begin{pmatrix}
\lambda_+ & 0 \\
0 & \lambda_-
\end{pmatrix} \).

Here, \( U \) is composed of the orthonormal eigenvectors of

![Figure A1. Equivalent circuit model for the stack electrode model in the trivial case](image)

![Figure A2. Equivalent circuit model for the stack electrode model at n = 2.](image)
\( M \), with eigenvalues \( \lambda_{+} \). To find the formal solution to 
\( \dot{X} = Y - MX \), note that \( U^{-1}X(t) = U^{-1}Y - DU^{-1}X(t) \)
is solved by \( U^{-1}X(t) = \exp[-Dt]a + D^{-1}U^{-1}Y \). The constant \( a \) is fixed by the boundary condition \( U^{-1}X(t) = 0 \),

\[
X(t) = U \begin{bmatrix}
1 - \exp\left(-\frac{\lambda_+ t}{2RC}\right) & 1 \\
0 & 1 - \exp\left(-\frac{\lambda_- t}{2RC}\right)
\end{bmatrix} \frac{1}{\lambda_-} U^{-1}Y.
\]

We see that the late-time relaxation of \( X(t) \) is determined by the smallest eigenvalue of \( M \). For the stack electrode system, the resistance scales linearly with the width of the respective electrolyte regions. Specifying to \( H = L \), we find \( R' = H/(2L) = 1/2 \). The eigenvalues of \( M \) then follow from \( (2 - \lambda)(2 - \lambda) - 2 = 0 \), which amounts to \( \lambda_{\pm} = 2 \pm \sqrt{2} \). We see that the long-time relaxation is determined by \( \tau = 2R'C/\lambda_- = RC/\lambda_- = (2 + \sqrt{2})\kappa^{-1}L/D \).

### 3. General \( n \) Case

We redraw Fig. 1(c) and introduce additional notation in Fig. A3. Similar to the previous subsection, the outer capacitor has a capacitance \( C \), while all inner capacitors have \( 2C \), as they mimic electrodes with electrolyte on either sides.

\[ Q_1(t) = 2C\Delta\Psi_1(t), \quad (A7a) \]
\[ Q_{n-1}(t) = 2C\Delta\Psi_{n-1}(t), \quad (A7b) \]
\[ Q_n(t) = C\Delta\Psi_n(t). \quad (A7c) \]

Kirchhoff states
\[ I = I_1 + I_{12}, \quad (A8a) \]
\[ I_{12} = I_2 + I_{23}, \quad (A8b) \]
\[ I_{(n-2)(n-1)} = I_{(n-1)} + I_{(n-1)n}, \quad (A8c) \]
\[ I_{(n-1)n} = I_n, \quad (A8d) \]

which gives \( I = I_1 + I_2 + ... + I_n \). For the different currents, Ohm’s law reads
\[ I_1 R' = 2[\Psi - \Delta\Psi_1(t)], \quad (A9a) \]
\[ I_{12} R' = \Delta\Psi_1(t) - \Delta\Psi_2(t), \quad (A9b) \]
\[ I_{23} R' = \Delta\Psi_2(t) - \Delta\Psi_3(t), \quad (A9c) \]
\[ I_{(n-1)n} R' = \Delta\Psi_{(n-1)}(t) - \Delta\Psi_n(t). \quad (A9d) \]

Combining the above equations gives \( n \) coupled differential equations.

Figure A3. Equivalent circuit model for the stack electrode model at \( n \).
Figure A4. The slowest relaxation time $\tau_n$ of a $n$-electrode model as obtained with the smallest eigenvalue $\lambda_-$ of the tridiagonal matrix $M$ [cf. Eq. (A11)]. The lines in (a) indicate the least-squares fit $\tau_n/\tau_{RC} = f_1 + f_2 n$ through the data up to $n = 250$. In (b) we then find the fits $f_1 = -1 - 0.91 H/L$, and $f_2 = 2 + 0.75 H/L$.

$$\Delta \Psi_1(t) = \frac{I_1}{2C} = \frac{I - I_{1/2}}{2C} = \frac{\Psi}{RC} - \left(\frac{1}{RC} + \frac{1}{2RC}\right) \Delta \Psi_1(t) + \frac{1}{2RC} \Delta \Psi_2(t),$$  \hspace{1cm} (A10a)

$$\Delta \Psi_2(t) = \frac{I_2}{2C} = \frac{I_{1/2} - I_{23}}{2C} = \frac{1}{2RC} \Delta \Psi_1(t) - \frac{1}{RC} \Delta \Psi_2(t) + \frac{1}{2RC} \Delta \Psi_3(t),$$  \hspace{1cm} (A10b)

$$\ldots$$

$$\Delta \Psi_n(t) = \frac{I_n}{C} = \frac{1}{R^C} \Delta \Psi_{(n-1)}(t) - \frac{1}{R^C} \Delta \Psi_n(t),$$  \hspace{1cm} (A10c)

$$\Delta \Psi_1(t = 0) = 0,$$  \hspace{1cm} (A10d)

$$\ldots$$

$$\Delta \Psi_n(t = 0) = 0.$$  \hspace{1cm} (A10e)

In matrix form this is

$$\begin{pmatrix} \Delta \Psi_1(t) \\ \Delta \Psi_2(t) \\ \vdots \\ \Delta \Psi_n(t) \end{pmatrix} = \frac{\Psi}{RC} \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} - \frac{1}{2RC} \begin{pmatrix} H/L(n-1) & -1 \\ 1 & 2 & -1 \\ \vdots & \vdots & \ddots & \vdots \\ -2 & -1 \\ -1 & 2 & -1 \end{pmatrix} \begin{pmatrix} \Delta \Psi_1(t) \\ \Delta \Psi_2(t) \\ \vdots \\ \Delta \Psi_n(t) \end{pmatrix},$$  \hspace{1cm} (A11)

which we again write as $\dot{X} = Y - MX$, where $M$ is now a tridiagonal matrix that is Toeplitz except for two elements ($M_{1,1}$ and $M_{n,n-1}$). Note that, for the top left element we used $H = h(n-1)$ to rewrite $R'/R = h/(2L) = H/[2L(n-1)]$ hence $1 + 2R'/R = 1 + H/[L(n-1)]$. Again diagonalizing $M$ as $M = U D U^{-1}$, the formal solution to (A11) reads

$$X(t) = U(1 - \exp[-Dt]) D^{-1} U^{-1} Y,$$  \hspace{1cm} (A12)

with

$$1 - \exp[-Dt] = 1 - \begin{pmatrix} \exp\left[\frac{-t\lambda_1}{2RC}\right] \\ \vdots \\ \exp\left[\frac{-t\lambda_n}{2RC}\right] \end{pmatrix}.$$  \hspace{1cm} (A13)

We used the above model to derive two key results of the main text. First, to obtain the data in Fig. 3(b) we diagonalized $M$ numerically for the case $n = 5$. With the resulting equivalent circuit potential differences
ΔΨ(t) encoded in X(t) [Eq. [A12]], we determine the surface charge densities $\Delta \sigma_i(t)$ to $C_i \Delta \Psi_i(t)$ on the electrodes of the stack electrode model. To do that, we use $C = A_{iK}$, $\Phi = e\Psi/k_B T$, and $X(t) = \Psi(t)$, to write $\sigma_i(t) = (k_B T e^2 \kappa^{-1}) \Phi f(t) = 2 \rho_{\kappa^{-1}} \Phi f(t)$. Results are shown in Fig. [2](b) with lines. In the same figure, we show numerical results of the PNP equation [Eqs. (1), (2), and (3)], with symbols. We see that, for $\Phi \ll 1$ and $\kappa L > \kappa h \gg 1$, the equivalent circuit model describes the behavior of the stack electrode model very well.

Second, to obtain Eq. (4), we proceed as follows. Writing $\lambda_n = \min\{\lambda_1, ..., \lambda_n\}$, the longest relaxation time reads $\tau_n = 2R' C / \lambda_n = \tau_{RC} \times 2H/[L(n-1)\lambda_n]$. We diagonalized $M$ numerically for various $n$ and $H/L$ to find $\lambda_n$. The resulting $\tau_n$, shown with symbols in Fig. [A4](a), can be accurately approximated by $\tau_n = \tau_{RC}(f_1 + f_2 n)$: for the three $H/L$ values considered, the residual of a least square fit was at most $R^2 = 0.00034$. In Fig. [A4](b) we see that the coefficients $f_1$ and $f_2$ are roughly linear in $H/L$. We performed a second least-squares fit to determine the coefficients $a_1, b_1, a_2, b_2$ in $f_1 = a_1 + b_1 H/L$ and $f_2 = a_2 + b_2 H/L$. Note, however, that we can determine $a_1$ and $b_1$ analytically. In the limit $H/L \to 0$, i.e., $R'/R \to 0$, all capacitors in Fig. [A4](a) are connected in parallel, yielding a total capacitance $C_{tot} = (2n-1)C$. Equation (A2) now applies, with $C$ replaced by $C_{tot}$. We find $\tau_n = \tau_{RC}(2n-1)$. This means that we need to constrain $a_1 = -1$ and $a_2 = 2$ when fitting $f_1$ and $f_2$. This ensures that, for $n = 1$ (for which $H/L = 0$), we correctly reproduce $\tau_1 = \tau_{RC}$. Fitting to $f_1$ and $f_2$-data at $n = 250$ [Fig. [A4](a)], we find $b_1 = -0.91$ and $b_2 = 0.75$ [Fig. [A4](b)]. Hence, the equivalent-circuit model predicts that all electrodes relax exponentially at late times with the same constant time

$$\frac{\tau_n}{\tau_{RC}} = \left(2 + 0.75 \frac{H}{L}\right) n - 0.91 \frac{H}{L}. \quad (\text{A14})$$

Figure [A5] is similar to Fig. [2](b), but we now show equivalent circuit predictions for $n = 250$ instead of $n = 5$. Shown also are the function $1 - \exp(-t/\tau_n)$ (blue) and the scaled total surface charge $\Sigma(t)/\Sigma_{eq}$ (red), with $\Sigma(t) = \sigma_1(t) + \sigma_2(t) + ... + \sigma_n(t)$ and $\Sigma_{eq} = \Sigma(t/\tau_{RC} \to \infty)$. Even though $\Sigma(t)$ harbors $n$ decaying exponential modes [related to all eigenvalues $\lambda_i$, see Eqs. (A12) and (A13)], we see that the total surface charge is approximated well by a single exponential decay with the longest relaxation time $\tau_n$. In other words, the stack electrode model suggests that $\tau_n$ gives a good estimate for the relaxation of the combined charge on all $n$ electrodes.

4. Relation to transmission line model

The circuit shown in Fig. [A3] differs from the transmission line model in one place: the capacitance of the $n$-th electrode is $C$ instead of $2C$. Tracing back the steps of the derivation in the previous subsection, we find that for the transmission line model, Eqs. (A7) and (A10), we obtain a factor 2 and 1/2, respectively. This yields the same differential equation $\dot{X} = Y - MX$ where $M$ is now given by

$$M = \frac{1}{2R' C} \begin{pmatrix} 1 + \frac{H}{L(n-1)} & -1 & \cdots & \cdots & -1 \\ -1 & 2 & -1 & \cdots & \cdots \\ \vdots & \ddots & \ddots & \ddots & \ddots \\ -1 & \cdots & -1 & 2 & -1 \\ -1 & \cdots & \cdots & -1 & 1 \end{pmatrix}. \quad (\text{A15})$$

With the same methods as before, one could determine the late-time relaxation timescale, whose $H/L \to 0$ limit now reads $\tau_n = 2n\tau_{RC}$ because $C_{tot} = 2C$ in this case.

Appendix B: Additional numerical PNP data

In the main text we presented numerical results for the PNP equation (B) and its initial and boundary conditions [Eqs. (1) and (2)] for $H/L = 1$ and several $\Phi$, $n$, $\kappa L$. In this section we present additional data for other parameters to reinforce some of the main conclusions of our analysis.

First, we discussed the case $\Phi = 0.001, \kappa L = 100$, $H/L = 1$, and $n = 5$. For the same parameters except $n = \{3, 6, 11\}$, in Fig. [B1] we present PNP data for the outer-electrode unit surface charge density $\sigma_n(t)$. Here, time is scaled either by $\tau_{RC}$ [Fig. [B1](a)] or by $\tau_n$ [Fig. [B1](b)]. The data collapse that we observe in the latter case again shows the value of the equivalent circuit model in describing the small-$\Phi$ relaxation of our setup.
Second, in Fig. 3 we studied the influence of \( \Phi \) and \( n \) on our setup through two parameter sets: \( \Phi = \{0.01, 0.1, 1, 2\} \), \( \kappa L = 100, H/L = 1 \), and \( n = 1 \); and \( \Phi = 2, \kappa L = 100, H/L = 1 \), and \( n = \{2, 3, 6\} \). We now use \( \Phi = 2, \kappa L = \{25, 50, 100\}, H/L = 0 \), and \( n = 1 \) to study the influence of \( \kappa L \). We show \( 1 - \sigma(t)/\sigma_{eq} \) with time scaled either by \( \tau_{RC} \) [Fig. B2(a)] or by \( L^2/D \) [Fig. B2(b)].

In the first case, \( 1 - \sigma(t)/\sigma_{eq} \) collapses at early times for different \( \kappa L \). This reinforces our finding of Fig. 3(c) where we found a similar early-time collapse for different \( \Phi \), from which we concluded that the early-time relaxation of \( 1 - \sigma(t)/\sigma_{eq} \) is described well by the equivalent circuit model. In the same figure [Fig. B2(c)] we saw that \( 1 - \sigma(t)/\sigma_{eq} \) relaxes on two timescales. We further investigate the second, slower timescale in Fig. B2(b), where time is scaled by \( L^2/D \). We see that \( 1 - \sigma(t)/\sigma_{eq} \) relaxes at late times with the same time scale for the different \( \kappa L \). To characterize both the early- and late-time response, we define a time-dependent function \( \tau(t) \),

\[
\tau(t) = -\left[ \frac{d\ln(1 - \sigma(t)/\sigma_{eq})}{dt} \right]^{-1}
\]

that, for a purely exponential charge buildup \( \sigma(t) = \sigma_{eq}[1 - \exp(-t/\tau)] \) yields \( \tau(t) = \tau^* \). Figure B2 presents \( \tau(t) \) for the same parameters as used in Fig. B1(a) and (b). At early times \( (t/\tau_{RC} < 1) \), \( \tau(t) = \tau_{RC} \), while at late times \( (t/\tau_{RC} > 1) \), \( \tau(t) \) shoots up to different plateaus \( \tau_{ad} \) for different \( \kappa L \). In Fig. B2(d) we plot \( \tau_{ad} \) against \( \kappa L \) for \( \Phi = 1 \) and \( \Phi = 2 \) and find a linear relation \( \tau_{ad}/\tau_{RC} = 0.1\kappa L \), hence \( \tau_{ad} = 0.1L^2/D \) (if \( n = 1 \)).

Third, as mentioned above, we discussed the case \( \Phi = 2, \kappa L = 100, H/L = 1 \), and \( n = \{2, 3, 6\} \). Here, we present additional data for the same \( \Phi \), \( \kappa L \), and \( H/L \) for \( n = \{2, 3, 6, 11, 21\} \). Notably, these values correspond to \( \kappa h = \{100, 50, 20, 10, 5\} \), which means that we probe the behavior of the stack-electrode model for both non-overlapping and overlapping EDLs. In Fig. B3(a) we see that \( 1 - \sigma(t)/\sigma_{eq} \) relaxes at late times with the same time scale for the \( n = \{2, 3, 6\} \), while for \( n = 11 \) and \( n = 21 \) (corresponding to \( \kappa h = 10 \) and \( \kappa h = 5 \)) it relaxes slower, arguably because EDLs overlap. The same conclusions hold for \( (c(t) - c_{eq})/(c(0) - c_{eq}) \), which we plot in Fig. B3(b). In Fig. B3(c) we plot the same data as in Fig. B3(a), but with time scaled by \( \tau_{ad} \) instead of by \( \tau_{RC} \). We see there that \( 1 - \sigma(t)/\sigma_{eq} \) collapses at early times for
Here, we reanalyze data of that paper for the decay of the data from (a). The dash line is a fit by eye: $Q = \{1.8[1 - \exp(-t/200)] + 0.1[1 - \exp(-t/9000)]\}$ C, whose two time constants were inspired by the dotted and dash-dotted lines in (a).

all $n$ considered, which again confirms the early-time $\tau_n$ scaling. For completeness, in Fig. 1(c), we again evaluated $\tau(t)$ as defined in Eq. (B1): similar to the $n = 1$ case, two plateaus appear.

**Appendix C: Comparison to experimental surface charge build up**

In the main text, we determined $\tau_n$ and $\tau_{ad}$ for parameters corresponding to the experimental setup of Ref. 25. Here, We reanalyze data of that paper for the decaying electric current $I(t)$ caused by an applied potential $\Psi = 0.3$. Repeated measurements were performed at different $\rho_b$: twice at $\rho_b = \{0.001, 0.01, 0.1\}$ M and four times at $\rho_b = 1$ M. Figure 1(a) shows the average currents $I(t)$ of those measurements for each $\rho_b$. Dotted and dash-dotted lines in Fig. 1(a) show two exponential decays with time constants $\tau_1 = 200$ s and $\tau_2 = 9000$ s. With these lines one sees for $\rho_b = 1$ M that $I(t)$ decays exponentially at late times, while at early times its behavior is more complicated. Figure 1(b) shows $Q(t) = \int_0^t I(t)$, determined numerically by integrating an interpolation through the data of figure Fig. 1(a).

Also shown with a dashed line is the function $Q(t) = \{1.8[1 - \exp(-t/\tau_1)] + 0.1[1 - \exp(-t/\tau_2)]\}$ C, where the numerical prefactors were fixed by eye. This dashed line describes $Q(t)$ properly after $t \approx 3000$ s, underestimating $Q(t)$ at earlier times. We saw in Fig. 1 that the stack electrode model displays a similar feature: at intermediate times, the total surface charge $\Sigma(t)$ is larger than $1 - \exp(-t/\tau_n)$. The difference between these two observables, however, is much smaller in the stack electrode model than in the experiments. Hence, our stack electrode model does not yet fully explain the experimental data of Ref. 25. Still, comparing the fitted time constants $\tau_1 = 200$ s and $\tau_2 = 9000$ s to $\tau_1 = 2.9 \times 10^2$ s and $\tau_2 = 4.8 \times 10^2$ s as stated in the main text, respectively, we see that our model predicts both timescales within approximately one order of magnitude. Even though we seem to predict $\tau_1$ better than $\tau_2$, using a smaller diffusion constant $D = 2 \times 10^{-10}$ m$^2$s$^{-1}$, to account for slow diffusion in pores [31 39], leads to $\tau_n = 2.3 \times 10^3$ s and $\tau_{ad} = 3.6 \times 10^3$ s and predictions for $\tau_2$ are better than for $\tau_1$.
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