Charging dynamics of an individual nanopore

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Meso-porous electrodes (pore width « 1 µm) are a central component in electrochemical energy storage devices and related technologies, based on the capacitive nature of electric double-layers at their surfaces. This requires that such charging, limited by ion transport within the pores, is attained over the device operation time. Here we measure directly electric double layer charging within individual nano-slits, formed between gold and mica surfaces in a surface force balance, by monitoring transient surface forces in response to an applied electric potential. We find that the nano-slit charging time is of order 1 s (far slower than the time of order 3 x 10^-2 s characteristic of charging an unconfined surface in our configuration), increasing at smaller slit thickness, and decreasing with solution ion concentration. The results enable us to examine critically the nanopore charging dynamics, and indicate how to probe such charging in different conditions and aqueous environments.

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Conducting materials with a large surface-to-volume ratio, such as meso-porous electrodes (pore widths ~1 μm), are important in a range of technologies1–6. Prominent among these are supercapacitors7,8, but also batteries9,10, fuel cells11,12, and electrocatalysts13,14, while emerging applications include capacitive deionization15,16, and the extraction of renewable energy through capacitive mixing of aqueous solutions of different salt concentrations17,18. Charge is stored in supercapacitors when electrolyte ions form (capacitive) electrical double layers (EDLs) at the surface of oppositely charged electrodes under an externally applied voltage19. Since the amount of charge stored is proportional to the available electrode surface area, materials with a high specific area (such as porous electrodes) are clearly at a premium; but they are only fully useful if ion transport enables equilibrium EDL formation over the entire pore within the relevant charging/discharging time. It is crucial therefore to be able to characterize and understand the dynamics of EDL formation within nano-pores.

In equilibrium, the EDL at a charged surface screens the associated electric field, with an exponential decay length (the Debye length) \( \lambda_D = \sqrt{\frac{e_0 \epsilon_0 k_B T}{\epsilon}} \) (for 1:1 electrolyte), where \( e_0 \) is the concentration of salt in the bulk solution, \( \epsilon_0 \) is the permittivity of free space, \( \epsilon \) is the dielectric constant, \( k_B T \) the thermal energy, and \( e \) the electronic charge18. Changes in the surface potential rearrange the ionic atmosphere comprising the EDL to a new equilibrium configuration19, a dynamic process known as EDL charging. This is well understood for planar electrodes in bulk solution, where the characteristic charging time is defined by \( \tau_C = \lambda_D^2 / H \) (where \( H \) is the distance between electrodes and \( D \) is the ion diffusion coefficient)19–22, but for the case of EDL charging in nano-confined geometries (as in porous electrodes) the dynamics may be much slower. This is because, in small diameter pores, changes to the EDL are constrained by the limited supply of ions within the pore23–27 and the time for ions to access the entire pore from the reservoir with which it is in contact.

A widely used description of ion transport in pores is the classic “Transmission-Line” (TL) model, by de Levie24,28, where the pore – a closed cylinder of length \( L_p \) and diameter \( h_p \) (\( L_p \gg h_p \gg \lambda_D \)) in contact with an ion reservoir - is treated as an equivalent TL circuit composed of a set of resistors and capacitors, yielding a time for EDL charging within the pore \( \tau_{TL} = (L_p^2 / D) \Lambda_D / h_p \). This characteristic time scales as the diffusion time (\( L_p^2 / D \)) for ions to traverse the pore length \( L_p \), modulated by the ratio (\( \Lambda_D / h_p \)). The latter is the extent of the near-surface EDL region (~\( \lambda_D \)), within which ion redistribution must occur due to the potential change, relative to the pore diameter \( h_p \), within which little overall change occurs. The charging dynamics of an EDL confined in a single nano-pore have been investigated primarily theoretically, e.g. refs. 6,29–33, while several treatments have extended the TL treatment, and different charging dynamics have recently been predicted for EDLs confined in dimensions comparable with its Debye length6,28,36. Experimentally, charging dynamics have been probed within (macroscopic) porous electrodes35,37–39, but to our knowledge, no measurements of EDL charging dynamics within a single nano-pore – the basic element of such electrodes – have been reported to date.

Here we use a surface force balance (SFB) to probe experimentally the charging dynamics of an EDL confined to a nano-slit between two surfaces, in response to a step-change in the surface potential (or charge) of one of them (arising from a step \( \Delta V_{\text{app}} \) in the potential applied to it). We find that the response to such a step is governed by two successive processes: Immediate formation of a strong electric field across the pore due to elimination of the screening, arising from the instantaneous charge imbalance in the EDL, followed by a slower process in which the ionic atmosphere of the EDL rebuilds to screen the generated electric field while charging the nano-pore interior (the gold acquires its new surface potential value over a time \( \delta t \) much faster than EDL charging time as it is associated with drift motion of electrons which is orders of magnitude faster than for ions in solution1,40). Our results show that full EDL charging within the nano-slit occurs over times of order 0.5 – 1 s, far longer than \( \tau_C = 3 \times 10^{-2} \) s in our configuration (where \( \tau_C = \lambda_D^2 / H \), and the values of \( \Lambda_D \), \( H \) and \( D \) are given below). They reveal that the charging time increases at smaller slit thickness, and decreases with increasing ion concentration in the electrolyte solution, suggesting that the process of EDL charging within the nano-slit is largely limited by diffusion of ions from the bulk reservoir to which the nano-slit is coupled12,28,36. These findings demonstrate the ability of the SFB to access and probe the EDL charging dynamics within a single nanoscale gap (~1 μm), the basic element of porous electrodes, providing a method for probing EDL charging in nano-confined slits with different surfaces and under different conditions.

**Results**

**Probing EDL charging in a nano-slit with the SFB.** Figure 1a shows a schematic of the experimental SFB configuration used in this study, where a single-crystal mica surface faces a smooth gold surface (r.m.s. roughness ca. 3 Å) at a controlled potential41–43. The absolute separation \( D \) between the surfaces is determined (to ±3 Å) by multiple beam interference and monitored via video-recording of the wavelengths of the interference fringes44,45.

We probe the perturbation and the charging of the EDL through its transient effect on the force between the gold and mica surfaces. A typical dynamic measurement, conducted in 5 mM NaNO3 (\( \Lambda_D = 4.3 \) nm), is shown in Fig. 1c. Initially, the surfaces are brought to a given initial separation \( D_0 (~ \lambda_D) \). Then, either a positive \((-0.2 \text{ V} \rightarrow +0.2 \text{ V})\) or negative \((+0.2 \text{ V} \rightarrow -0.2 \text{ V})\) potential step \( \Delta V_{\text{app}} \) is applied to the gold while monitoring the gold-mica separation \( D \) (Fig. 1c). After \( \Delta V_{\text{app}} \) is applied at time \( t = 0 \) (Fig. 1d), the gold electrode – both outside and within the confined nano-slit – accumulates a new surface charge density over a very short time \( \delta t \) (typically \( < 10^{-9} \) s due to drift motion of electrons1,40) as it attains its new surface potential value \( \Psi_{\text{gold}} \). This generates \((\delta t)\) an unscreened electric field19 which exerts an electrostatic force \( F_c(t = \delta t \approx 0) \) on the negatively charged mica, bending the spring \( k_n \) on which it is mounted by \( AD \) to an extremal separation \( D_1 \) relative to the gold, over a time \( \Delta t_e \). As ions transport to reconstruct the EDL (EDL charging) within the nanopore, \( F_c \) is progressively screened and the surfaces relax to their initial separation \( D_1 \) over a further time \( \Delta t_c \) (Fig. 1d), since, in all cases in our study, \( D_1 \gg \lambda_D \). This transient motion manifests as a peak, with a characteristic asymmetric shape, in the \( D \) vs. \( t \) trace (Fig. 1d) and a period of \((\Delta t _e + \Delta t_c) \approx 0.85 \) s was obtained in response to a potential step of \(-0.2 \text{ V} \rightarrow +0.2 \text{ V} \). Overall, this indicates three different time scales following the potential step: \((\Delta t _e + \Delta t_c) \gg \tau_C \gg \delta t \). Thus, the times \((\Delta t _e + \Delta t_c)\) we measure in our experiments, corresponding to the EDL equilibration within the nano-pore, are well separated from \( \tau_C \), the time for EDL equilibration at the unconfined gold away from the nanopore.

The initial \((t = 0)\) instantaneous electric field across the gap depends on the effective surface potentials \( \Psi_{\text{gold}} \) at the gold surface at different applied potentials \( \Delta V_{\text{app}} \); these may be extracted from normal force vs. surface-separation \( D \) profiles, as shown in...
Transient forces during EDL charging. The force $F_e(t)$ attracts the charged mica surface due to the induced positive charge on the gold surface, changing the surface separation $D_i$ by $\Delta D(t) = (D_i - D(t))$. This motion is opposed by the bending of the spring (of constant $K_n$) on which the mica surface is mounted, which exerts an opposing force $F_k = K_n \Delta D$, and by a hydrodynamic damping force $F_H$ (arising from extrusion of the liquid as the surfaces approach or separate). Van der Waals (vdW) attraction between the surfaces is negligible since $D$ is always $> 20\text{ nm}$, and we may set the normal surface force as equal to $F_k$. The equation of motion is thus $F_e(t) = F_k + F_H + m(d^2D/dt^2)$, where the last term is inertial and $m$ is the mass of the mica surface and its mount. We note that the magnitude of $m(d^2D/dt^2)$ (where $m = 3 \times 10^{-3} \text{ kg}$), as determined from the $D$ vs. $t$ plots (Fig. 1d or Fig. 2b), is ca. $10^{-9}\text{ N}$, which is negligible compared with the hydrodynamic ($F_H = O(10^{-6}\text{ N})$) and spring ($F_k = O(10^{-4}\text{ N})$) force terms, and may be ignored. The hydrodynamic force, between a sphere approaching a flat a closest distance $D$ away across a liquid of viscosity $\eta$, is

$$F_H = 6\pi R^2 \eta ([dD/dt]/D),$$

and the equation of motion becomes:

$$F_e(t) = K_n \Delta D(t) + 6\pi R^2 \eta ([dD/dt]/D)$$

(1)

Before solving equation 1, we address an important qualitative point concerning the EDL charging. Following the potential change on the gold surface at $t = 0$, $F_k$ is a maximum but immediately begins to decay as the EDL recharges. During the initial motion ($t < \Delta t_s$) $F_k$ exceeds $F_k$, but at $t = \Delta t_s$, where $D = D_i$ (Fig. 1d), it has decayed so that $F_e(\Delta t_s) = F_k = K_n (D_i - D)$. At longer times $t > \Delta t_s$, $F_k$ becomes smaller than the spring force $F_k$, and the mica surface is pushed back towards its equilibrium position $D = D_i$ over the period $\Delta t_s$. The crucial point is whether the period $\Delta t_s$ is due to hydrodynamic damping alone, or to a slower process due to $F_k$ decay arising from increased screening associated with EDL charging limited by ion transport within the gap. To resolve this we solve for the motion of the surfaces from $D = D_i$ at the peak to $D = D_o$ on the assumption of hydrodynamic damping alone. The relevant equation is simply equation (1) with $F_e$ set to zero, and boundary condition $D = D_i$ at $t = 0$. The resulting $D(t)$ variation is given in Fig. 3 and shown as the red curves in Fig. 3a. We see that for traces at
EDL charging time but leaves the hydrodynamic damping time unchanged, so that it becomes more dominant at the smallest \( D_i \) values such as \( D_i < \text{ca. } 80 \text{ nm} \). This is also manifested in the \( \Delta D \) vs. \( D_i \) plot (Supplementary Figure 1) as a decrease in \( \Delta D \) at \( D < \text{ca. } 80 \text{ nm} \). To solve equation (1), we require an explicit form for \( F_s(t) \). We approximate the instantaneous initial force (just after application of the potential change on the gold surface) as

\[
F_s(0) = \pi R e_0 (\Delta \psi_{\text{eff}})^2 / D(t = 0),
\]

which is the force between a conducting sphere (radius \( R \)) and a conducting plane a closest distance \( D \) apart\(^{17} \) (\( D \times R \)) differing in potentials by \( \Delta \psi_{\text{eff}} \). In our configuration \( \Delta \psi_{\text{eff}} = \psi_{\text{gold,eff}} - \psi_{\text{mica}} \) (at \( t = 0 \), the effective potential difference at \( t = 0 \) between the opposing gold and mica surfaces, where \( \psi_{\text{gold,eff}} \) is the instantaneous effective gold surface potential (\( t = 0 \)) arising from the abrupt variation of the gold surface charge (Supplementary Note 1). This may be evaluated from the potentials extracted from the force vs. distance profile at the relevant applied potentials\(^{44} \), Fig. 2a. The decay with time of \( F_s(t) \) is complex, depending on flux of ions between the bulk and the nano-slit which in turn modifies the initial gold surface charge (i.e. at \( t = 0 \)) within the confined area until the EDL is fully relaxed. To proceed, we may assume that \( F_s \) decays exponentially with a characteristic time \( \tau \) due to the progressive screening of the electrostatic force with time, as the near-surface ion concentration rearranges following the potential change. Equation (1) then becomes:

\[
\left[ \pi R e_0 (\Delta \psi_{\text{eff}})^2 / D(t) \right] e^{-t/\tau} = K_e \Delta D(t) + 6 \pi R^2 \eta [(dD/dt)/D(t)]
\]

(2)

We seek an approximate solution by recognizing that \( D \) does not change too greatly from \( D_i \) during the transient response (particularly for the larger \( D_i \) values), and replace \( D \) by \( D_i \) in the denominators of the terms for \( F_s \) and \( F_s(t) \). This gives:

\[
\left[ \pi R e_0 (\Delta \psi_{\text{eff}})^2 / D_i \right] e^{-t/\tau} = K_e \Delta D(t) + 6 \pi R^2 \eta [(dD/dt)/D_i]
\]

(2')

which for boundary condition \( D = D_i \) at \( t = 0 \), solves as:

\[
D(t) = D_i + \left[ F_s(0) e^{-t/\tau} \right] \left( \exp(t (f_{i1} - K_e \tau) / f_{i1}) - 1 \right) / (K_e \tau - f_{i1}),
\]

(3)

where \( F_s(0) = \pi R e_0 \Delta \psi_{\text{gold,eff}}(\Delta \psi_{\text{gold,eff}})^2 / D_i \) and \( f_{i1} = 6 \pi R^2 \eta / D_i \).

Equation (3) describes the transient change in \( D \) in response to \( \Delta \psi_{\text{app}} \). We note that at the peak in \( D(t) \), at \( t = \Delta t_0 \), \( (dD/dt) = 0 \) so that for this value of \( t \) (\( = \Delta t_0 \)), equation (2') yields the value of \( \tau \) directly. This may then be used in the expression for \( D \) (equation 3)). In Fig. 3b, this is done for the \( D \) vs. \( t \) traces at different \( D_i \) values, showing a close quantitative fit with no adjustable parameters (all parameters are determined, Fig. 3). We confirmed the validity of our approximate solution by numerically solving equation (2) (Supplementary note 4). The numerical solution shows the behavior of \( D(t) \) to be close to that predicted by equation (3) over the range of \( D \) values in our experiments, and as expected, closest at higher \( D \) values where the approximation leading to equation (3) is best (Supplementary Figure 3).

**Effect of confinement on EDL charging time.** In Fig. 4 we gather together results for the EDL charging times for different \( D_i \) values, that is, different thicknesses of the nano-slit, showing the variation with \( D_i \) of \( \Delta t_n = \Delta t_0 \) and \( (\Delta t_{i0} = \Delta t_e) \) (inset to Fig. 4a). While the values shown are for \( \Delta \psi_{\text{app}} = -0.2 \text{ V} \rightarrow +0.2 \text{ V} \) and \( +0.2 \text{ V} \rightarrow -0.2 \text{ V} \) in 2 mM salt, similar behavior is seen at different salt concentrations (Fig. 4b), and for different salts (Fig. 4c), as well as for other potential variations (Supplementary note 3). In Fig. 4a
Mechanism of nano-slit charging. It is of interest to consider the EDL charging dynamics in the context of the classic transmission line (TL) approach noted earlier.\textsuperscript{2,28} In our configuration (Fig. 1b), the nano-pore or nano-slit is the gold-mica gap about the region of closest approach, $D = D_0$, strictly the region between two crossed cylinders of mean radius $R$. Its effective geometry – as in the Derjaguin approximation,\textsuperscript{18} which is valid for $D_i = R$ in the present case – is that of a circular slit bounded by a spherical surface and a flat, with a slit radius $r = L$, in contact with an ion reservoir (because the slit is formed by two orthogonal cylindrical surfaces, it is symmetric about its midplane). $L$ is the distance required by ions from the reservoir (at $r = L$) to fully permeate the pore to its center ($r = 0$), where its thickness is $h_p = D_i$, to compensate for the charge induced on the gold by the potential step $\Delta \Psi_{app}$. Within the TL model, the characteristic charging time of the EDL within such a circular slit is then expected to scale as $\tau_{TL} = (L^2 / D)(\lambda_D / h_p)^{1/2}$,\textsuperscript{2,24} The surface separation at $r = L$, $D = D_i + (L^2 / 2R)$ (Fig. 1b), must be sufficiently large to provide for the required excess of ions. This corresponds to a value $L \approx (2R \Delta \sigma / \epsilon_0 \sigma)^{1/2}$ (Supplementary note 2), where $\Delta \sigma$ is the change in the gold surface charge density arising from $\Delta \Psi_{app}$. In Fig. 4b, it is shown as a solid blue curve, the characteristic time $\tau_{TL} = (L^2 / D)(\lambda_i / h_p)$ expected for a pore of length $L$, and width $h_p = D_i$. The fit to the experimental data corresponds to $L = 150 \mu$m. This is within a factor 2 of the value $L = (2R \Delta \sigma / \epsilon_0 \sigma)^{1/2} \approx 87 \mu$m evaluated for the corresponding potential step ($\Delta \Psi_{app} = +0.2$ V $\rightarrow$ $-0.2$ V in $2 \text{mM}$ salt) (Supplementary Note 2), which is believed to arise from the different geometries considered in the two cases. The characteristic time $\tau_{TL} = (L^2 / D)(\lambda_D / h_p)$ also predicts that EDL charging is faster for higher salt concentrations, since (in our configuration) a larger $\epsilon_0$ is associated both with a smaller $L$ ($\sim \epsilon_0^{-1/2}$), as well as a smaller $\lambda_D$ ($\sim \epsilon_0^{-1/2}$), suggesting $\tau_{TL} \sim \epsilon_0^{-3/2}$. This is indeed observed for EDL charging from higher salt concentrations as shown in Fig. 4b, where the experimental charging time is roughly 3.5-fold larger in the $2 \text{mM}$ NaNO$_3$ salt compared with the $5 \text{mM}$ salt, similar to the expected ratio ($\epsilon_0 = 2 \text{mM} / \epsilon_0 = 5 \text{mM}$)$^{3/2} \approx 4$. In addition, we would expect from the expression for $\tau_{TL}$ that ions with different diffusion coefficients $D$ would result in different charging times. Additional cations need to permeate the slit from the reservoir when the applied potential change renders the surface charge more negative (e.g. $\Delta \Psi_{app} = +0.2$ V $\rightarrow$ $-0.2$ V), and additional anions need to permeate for the opposite case. For the NaNO$_3$ salt, Fig. 4a, b, where the $D$ values for Na$^+$ ($D = 1.3 \times 10^{-9}$ m$^2$ s$^{-1}$) and NO$_3^-$ ($D = 1.9 \times 10^{-9}$ m$^2$ s$^{-1}$) differ by some 40%, there is a slight indication that EDL charging is slower when $\Delta \Psi_{app} = +0.2$ V $\rightarrow$ $-0.2$ V (red squares in Fig. 4a, when it is controlled by transport of slower Na$^+$ ions) relative to $\Delta \Psi_{app} = -0.2$ V $\rightarrow$ $+0.2$ V (green squares, when charging occurs by transport of NO$_3^-$ ions). However, when NaNO$_3$ is replaced by LiClO$_4$, where the $D$ values for the latter ($1 \times 10^{-9}$ m$^2$ s$^{-1}$ and
where ionic transport rather than hydrodynamic effects dominate the dynamics (see Figs. 3a and red curve in 4a); indeed, the difference between the charging times for anionic vs. cationic transport demonstrates clearly that the decay of the transient forces that we measure is dictated by diffusive-transport of ions from the reservoir. Finally, we would expect that different potential steps would result in a different charging times through their effect on the surface charge density change \( \Delta \sigma \) and hence on the characteristic time \( \tau_D \), as indeed is seen (Supplementary Figure 2). Thus, this broad agreement of the absolute magnitude as well as the variation of the predicted charging times \( \tau_D = (L^2/D)(\lambda_D/\sigma) \) with our measured EDL charging for different slit widths, salt concentrations, ionic mobility and surface potential changes, indicates the validity of the TL concept and its scaled behavior for our system.

**Discussion**

In summary, we report the first measurements of EDL charging dynamics within a single nano-confined circular pore (or slit) following a step change in the surface potential (and charge) of one of the confining surfaces. This is done, using an SFB, by monitoring the transient change in surface forces due to an instantaneous electric field arising from the EDL perturbation, which decays as the EDL charges. Our results are in line with the characteristic times expected from the transmission line model applied to our nano-slit geometry, and indicate that such an approach could be used for probing EDL charging dynamics within single nano-slits in different conditions and aqueous environments.

**Methods**

**Materials.** Gold pellets, 99.999% pure, were purchased from Kurt J. Lesker and evaporated from a graphite crucible. Sodium nitrate, NaNO\(_3\), 99.99% pure was purchased from Merck Millipore and used as received. Lithium perchlorate, LiClO\(_4\), 99.99% pure was purchased from Sigma-Aldrich and used as received.

**Preparation of salt solutions.** NaNO\(_3\) and LiClO\(_4\) were dissolved in purified water with a total organic content of less than 1 ppb (TOC < 1), a resistivity of 18.2 M\(\Omega\) cm and pH = 5.8.
Surface force balance experiment. An atomically smooth back silvered mica and molecularly smooth gold surface are glued to cylindrical fused-silica lenses (curvature radius \( R = 1 \) cm) in a crossed-cylinder configuration, equivalent to the geometry of a sphere on a flat, with the lower lens (mica) mounted on a horizontal leaf spring (spring constant \( K = 81.5 \pm 2.7 \text{N m}^{-1} \)) and the top lens (gold) mounted on a sectored piezoelectric tube (PZT). The gold surface, serving as a working electrode (W), is connected to a potentiostat together with two platinum wires, acting as reference (R) and counter (C) electrodes, as described in detail elsewhere\(^{44,45}\). During all measurements, the electrodes are immersed in an electrolyte solution inside a quartz bath, custom-designed to prevent leakage of current to the ground, and the distance \( H \) between them is of order a few mm. The distance between the surfaces is measured with a resolution of \( 1.0 \pm 0.3 \) nm using multiple beam optical interferometry, and the normal forces between the surfaces are monitored through the bending of the horizontal spring and measured via a dynamic approach with a force sensitivity of \( \pm 50-100 \text{nN} \), as previously described in detail\(^{46,49}\).

Video capture and analysis. The absolute surface separation between the surfaces during EDL charging and dynamic force measurements was continuously monitored, by capturing the fringes of equal chromatic order (FECO) position, using a fast video recording camera (SONY XC-HR70) with a frame rate of 60 frames per s. In our gold/medium/mica/silver two-layer interferometer system each pixel is equivalent to an absolute distance of ca. \( 0.2-0.3 \) nm. The separation between the surfaces was determined using the multilayer matrix method, as previously described in detail\(^{50,51}\).

Data availability. The data sets generated and analyzed during the current study are available from the corresponding author on reasonable request.

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Author contribution

J.K., R.T. and G.S. conceived the idea and designed the experiments. R.T. conducted the experiments and analyzed the data. S.S. and P.P. assisted with theoretical aspects of EDL charging dynamics. R.T. and J.K. wrote the manuscript. All authors discussed the results and commented on the manuscript.

Additional information

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