Corrigendum: Superionic state in double-layer capacitors with nanoporous electrodes

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S Kondrat and A Kornyshev

Department of Chemistry, Faculty of Natural Sciences, Imperial College London, SW7 2AZ, UK

E-mail: s.kondrat@imperial.ac.uk and a.kornyshev@imperial.ac.uk

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There is a misprint in the numerical pre-factor on the right-hand side of equation (2). Instead of $1/\sqrt{2}$ one should read $4/\sqrt{2}$.

Equation (2) is an asymptotic form of equation (1). The purpose of presenting equation (2) was to show that the electrostatic interaction between point charges inside a slit-like, metallic nanopore decays exponentially with the ‘lateral’ distance between the charges, and that its decay length is equal to the pore width divided by $\pi$.

No results of the paper are affected by the misprint, since the correct equation (1) has been used in all calculations.
FAST TRACK COMMUNICATION

Superionic state in double-layer capacitors with nanoporous electrodes

S Kondrat\textsuperscript{1,2} and A Kornyshev\textsuperscript{1}

\textsuperscript{1} Department of Chemistry, Faculty of Natural Sciences, Imperial College London, SW7 2AZ, UK
\textsuperscript{2} Max-Planck-Institut für Mathematik in den Naturwissenschaften, D-04103 Leipzig, Germany

E-mail: skondrat@ic.ac.uk and a.kornyshev@imperial.ac.uk

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Abstract
In recent experiments (Chmiola \textit{et al} 2006 \textit{Science} \textbf{313} 1760; Largeot \textit{et al} 2008 \textit{J. Am. Chem. Soc.} \textbf{130} 2730) an anomalous increase of the capacitance with a decrease of the pore size of a carbon-based porous electric double-layer capacitor has been observed. We explain this effect by image forces which exponentially screen out the electrostatic interactions of ions in the interior of a pore. Packing of ions of the same sign becomes easier and is mainly limited by steric interactions. We call this state ‘superionic’ and suggest a simple model to describe it. The model reveals the possibility of a voltage-induced first order transition between a cation(anion)-deficient phase and a cation(anion)-rich phase which manifests itself in a jump of capacitance as a function of voltage.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Electric double-layer supercapacitors (EDLCs) have recently attracted considerable attention due to their high energy density and fast power delivery [1–4]. The carbon-based EDLCs store energy at the electrolyte/carbon interface. In order to increase the amount of energy stored it is necessary to increase the carbon surface area. This is usually achieved by using highly porous carbon materials, with the pore size being twice the size of the ions so as to allow ions adsorption on both pore walls [5, 4].

In recent experiments [6, 7] Gogotsi \textit{et al} have measured the capacitance per surface area of EDLCs with nanoporous carbon-based electrodes versus the pore width. They obtained a surprising result: an anomalous increase of the capacitance with decreasing pore width for nano and subnano pores comparable in size with the size of bare ions. Both an organic electrolyte [6] and a (solvent-free) ionic liquid [7] have been tested as an electrolyte medium leading to the same effect.

Molecular dynamics (MD) simulations have confirmed the experimental results [8, 9]. For instance, in [9] the simulations have been performed for EMI cations and TSFI anions as ionic liquid and the interior of a single-wall carbon nanotube (CNT) as pore. The ‘anomalous’ increase of the capacitance has been observed for the CNT radii down to the ion’s size.

It has been proposed that partial desolvation of the ions entering small pores is responsible for the anomalous behaviour of the capacitance in the case of organic electrolytes [6]. A recently considered electric wire-in-cylinder model [10, 11] offers a good fit to the experimental data but for further development of the porous EDLCs it is important to understand the underlying physics of the capacitance in nanopores.

In this fast track communication we propose a simple explanation of the anomalous capacitance behaviour by introducing the concept of a superionic state in a metallic nanopore caused by (i) exponential screening of the ion–ion pair interactions in a nanogap, which arises due to the image forces and enables more ions of the same sort to occupy the pore. By the same token, there is also (ii) an electrostatic contribution to the free energy of transfer of ions from the bulk to the pore interior. The latter tends to increase the ion density.
in a pore, compensating the opposing trend due to the loss of the solvation shell by the ions moving into the pore.

2. Model

Let us consider a point charge at \( z = z_1 \) confined between two metal plates (cf figure 1 with \( V = 0 \)). The electrostatic potential created by this charge, which satisfies the Laplace equation and Dirichlet boundary conditions at the plates, can be easily found using the Fourier–Bessel transform to give

\[
\phi(z, R; z_1) = \frac{4}{\varepsilon L} \sum_{n=1}^{\infty} \sin(\pi n z_1/L) \sin(\pi n z/L) \times K_0(\pi n R/L),
\]

where \( \varepsilon \) is the dielectric constant of a medium between the plates, \( R \) is the lateral distance from the charge, \( L \) is the plates separation (i.e., the pore size), and \( K_0(x) \) is the modified Bessel function of the second kind of order \( n \). Using the asymptotic behaviour of \( K_0(x) \) for \( x \gg 1 \) one finds for \( R \gg L/\pi \)

\[
\phi(z, R; z_1) \approx \frac{e^{-\pi R/L}}{\varepsilon \sqrt{2L}} \sin(\pi z_1/L) \sin(\pi z/L),
\]

which means that the electric potential exponentially decays with the distance in the plane parallel to the charge, and the Coulomb interaction between two charges is effectively screened out. In the opposite limit of large \( L \gg \pi R \), equation (1) recovers the Coulomb law.

We consider for simplicity a single, metallic\(^3\), slit-like\(^4\) pore, infinitely extended in the lateral directions (see figure 1), and neglect the boundary effects at the ‘entrance’ and ‘exit’ or closing of the pore (for supercapacitor electrodes the typical pore length is usually much longer than its width). The electrostatic potential at the pore walls is measured with respect to the reference electrode in the ‘bulk’ of the capacitor. We consider a small nanoscale pore, in which there is room only for one ionic layer (as in the experiments and simulations). Furthermore, we assume for simplicity that the ions are situated on average in the middle of the pore (i.e., \( z = L/2 \), cf equations (3) and (4)). Although not generally true, this assumption should not qualitatively change our conclusions.

Now using equation (1), and taking the voltage into consideration, one finds for the internal energy (per surface area) due to electrostatic interactions of an ionic liquid in a pore

\[
\beta U(\rho, c) = \beta eVc + 4c^2 R_c(\rho) L_B \sum_{m=1}^{\infty} \frac{\sin^2(\pi m/2)}{m} \times K_1(\pi m R_c(\rho)/L),
\]

where \( \beta = 1/k_B T \), with \( k_B \) being the Boltzmann constant and \( T \) the temperature, and where \( L_B = \beta e^2/\varepsilon \) is the Bjerrum length\(^5\); \( c = Z_+\rho_+ - Z_-\rho_- \) and \( \rho = \rho_+ + \rho_- \) are the two-dimensional charge density and total density of the ions in the pore, respectively, where \( \rho_\pm \) are the (two-dimensional) densities of the \( \pm \) ions and \( Z_\pm \) the corresponding valencies. In the derivation of equation (3) we have used the cut-out disk approximation [14] with the cut-out radius \( R_c(\rho) = \sqrt{\pi \rho}^{-1/2} \). The voltage, which appears linearly in equation (3), drives the anions to and cations from the pore for \( V > 0 \), and vice versa for \( V < 0 \).

We present the free energy of transfer of an ion from the bulk into a pore as a sum of two contributions: (i) a ‘resolvent’ free energy \( \delta E_\alpha(\alpha = \{+, -\}) \) due to the (partial) loss of the solvation shell when an ion moves from the bulk to the pore, which we assume to be \( L \)-independent, and (ii) a change in the self-energy of an ion due to confinement, which characterizes its interaction with the metal plates. The latter can be approximated as the work of ‘charging’ of a point charge inside the pore minus the work needed to charge it in the bulk with the same dielectric constant: \( (q^2/2) \lim_{r \to r_+} (\phi_L(r, r_1) - \phi_L = \infty(r, r_1)) \).

\(^3\) In the experiments of [6, 7] carbide-derived carbon (CDC) materials have been used for electrodes. The CDCs are characterized by properties close to those of metals, in particular to a high relative conductivity. In our work we use the simplest approximation, assuming that the pore walls are perfect conductors so that the electric field vanishes inside the walls. For semi-metals, like graphite, the electric field penetrates the walls and decays exponentially there [13]. In the present context it means that the wall separation will be, loosely speaking, effectively shifted by some small \( \delta L > 0 \), which will slightly weaken the effects discussed here; however, the screening of the electric field by thin carbon walls deserves a special investigation.

\(^4\) Cylindrical pores have been used in the experiments and simulations [6–9]. In a cylindrical pore the effect of screening is even stronger than in a slit pore. A slit pore, in turn, is a first approximation for connected-pore geometries (such as the space between nanotubes), and can also be beneficial for fast charging/discharging dynamics.

\(^5\) The Bjerrum length is the distance between two charges at which their Coulomb interaction energy in a medium of a given dielectric constant \( \varepsilon \) is equal to the thermal energy. The value of the Bjerrum length in the bulk is of the order of 5 nm for a typical ionic liquid and 0.7 nm for an aqueous electrolyte solution at room temperature. In nanopores the dielectric constant is reduced, being determined by an effective polarizability of a quasi two-dimensional layer of ions. Its value is not known, but we expect it to be in the range between 2 and 5, which gives the Bjerrum length between 11 and 28 nm.
one obtains for this contribution to the internal energy (per surface area)

\[ \beta E_s(\rho_\pm) = \sum_{a=\pm} \left( \beta \delta E_a - \frac{L_B}{L_f} (1/2) \rho_a^2 \right) \rho_a, \]

where

\[ f(x) = \int_0^\infty \left( \frac{1}{2} - \frac{\sinh(Q(1-x)) \sinh(Qx)}{\sinh(Q)} \right) dQ. \]

The function \( f(x) \) is positive-definite around \( f(x = 1/2) = \min_{x\in[0,1]} f(x) = \ln(2) \), and hence the second term in equation (4) is negative. The resolution energy \( \delta E_\pm \) is positive and depends on the type of electrolyte medium; its value is not known exactly, but we estimate it to be not larger than \( 20k_B T \) (such an estimate can be obtained by combining the methods of calculation of solvation energy in condensed media [15] and typical forms for nonlocal dielectric function of ionic liquids that account for overscreening [16]). This implies that for sufficiently large \( L_B/L \) the total free energy of transfer is negative, and will therefore favour an increase of the ion densities inside the pore relative to the bulk (irrespective of the voltage and the sign of the charges).

The total free energy of an ionic liquid in the pore (per surface area) is

\[ F = U + E_s + \sum_{a=\pm} \mu_a \rho_a - TS, \]

where \( S \) is the entropy and \( \mu_a \) chemical potentials. For the ions of the same size \( d \) the entropy is given by [17–19]

\[ S = -k_B \left( \sum_{a=\pm} \rho_a \ln \left( \frac{\rho_a v_0}{L} \right) + \frac{L}{v_0} \left( 1 - \frac{\rho_{\pm}}{L} \right) \right), \]

where \( v_0 = \pi d^3/6\eta_m \) is the minimal volume per ion and \( \eta_m \) the maximum packing fraction (\( \eta_m = \pi/6 \) for a close-packed simple cubic lattice and \( \sqrt{2} \pi \sqrt{3}/6 \) for a face-centred cubic or hexagonal lattice, and \( \eta_m \approx 0.64 \) for random close-packing, see e.g. [20]). We use \( \eta_m = \pi/6 \) here and note that other values of \( \eta_m \) will merely shift the capacitance curves and locations of the transitions discussed here but shall not lead to any qualitative changes.

The first term in equation (7) corresponds to the entropy of ions, and the last term is the entropy of a solvent (if there is one). Note that equation (7) reflects the three-dimensionality of the problem. We allow the total density to exceed the maximum two-dimensional density and limit its value by \( L/v_0 \) instead. In this way we mimic possible deviations of the ion locations from the middle of the pore, and note that the effects discussed below do persist if we use the fully two-dimensional entropy, but the values obtained are of course different. Finally, the chemical potentials \( \mu_\pm \) are set to the chemical potentials of the ionic liquid in the ‘bulk’, i.e., where the electric potential vanishes (we recall that, besides here, the bulk part does not appear in the model). Hence

\[ -\beta \mu_\pm = \ln \left( \frac{v_0 \bar{\rho}_\pm}{1 - v_0 \bar{\rho}_\pm} \right) = \ln \left( \frac{\gamma Z_\pm}{Z(1-\gamma)} \right), \]

where \( Z = Z_+ + Z_- \), \( \bar{\rho}_\pm = \bar{\rho}_\pm^{(\infty)} \) is the total (three-dimensional) density of the ions in the bulk, \( \gamma = v_0 \bar{\rho}_\infty \) (see [17, 18]), and we have used the electro-neutrality condition obeyed in the bulk.

The free energy (6) can now be minimized numerically with respect to the ion densities \( \rho_\pm \), and the differential capacitance can be found by numerically differentiating the negative of the total charge accumulated in the pore with respect to the voltage.

### 3. Results and discussion

The capacitance (per surface area) versus the pore width is shown in figure 2(a) for a few values of the voltage \( V \). At zero voltage the capacitance increases with decreasing pore width (solid line in figure 2(a)), in agreement with the experimental observations [6, 7]. Note that \( C > C_B \) for small pore widths, where \( C_B = \varepsilon/2\pi d \) is the Helmholtz capacitance.
the double-layer capacitance has recently been reported for glassy electrolytes and planar electrodes [21], and has been claimed to result from the reduced ion–ion interactions at the surface [22]. We note, however, that in nanogaps such a reduction is exponential and has different manifestations. Obviously, $C \equiv 0$ for pores smaller than the ion size because the ions cannot enter the pore (not shown in figure 2). The differential capacitance also vanishes for voltages higher than a certain threshold voltage $V_0$ (see figure 2(b) and dot–dash line in figure 2(a)); this is because the pore is fully occupied by anions for $V > V_0$.

For larger pores and intermediate voltages we observe a jump in both capacitance versus pore size and capacitance versus voltage curves (dashed lines in figure 2). It marks the onset of a first order phase transition. This transition occurs when the applied voltage (positive in this case) is sufficiently high to drive the cations out of the pore but is not yet high enough to fill the pore completely with anions. In other words, the transition separates a cation-deficient (CD) phase and a denser cation-rich (CR) phase. (In the case $V < 0$ the transition separates the anion-rich (AR) and anion-deficient (AD) phases.) This is demonstrated in figure 3(a), where we plot the cation density $\rho_+$ versus voltage. At $L/d = 1.2$ the density profile $\rho_+(V)$ is discontinuous, manifesting a first order transition. At smaller $L/d \approx 1.08$ the profile is continuous, but $d\rho_+/dV$ diverges at $V/V_T \approx 24.8$, which indicates a critical end-point. The corresponding phase diagram in the (voltage, pore size) plane is shown in figure 3(b).

The CR/AR phases are characterized by a high total ion density close to $\rho_{\text{max}} = L/v_0$ (see figure 3(a)). This is due to the superionic state created in the pore interior, i.e., the favourable free energy of transfer (see equation (4)) and the exponential screening of the Coulomb interactions (see equations (2) and (3)). The pore charging in this case is mainly due to the exchange of the cations in the pore with the anions from the outside of the pore (for $V > 0$) such that the total density remains practically constant (see figure 3(a)). This is to be contrasted with the charging in the CD and AD phases, which is essentially characterized by an increase of the total ion density. Therefore, the phase transition lines also separate two different ‘charging regimes.’ It is reasonable to expect the charging/discharging dynamics also to be different in these two regimes, which may be of considerable importance for power delivery of porous EDLCs.

4. Conclusions

We have considered a simple phenomenological model in order to understand the properties of EDLCs with nanoporous electrodes. Our model takes into account the exponential screening of the ion–ion interactions in a metallic nanopore and the interaction of ions with pore walls—both determined by image forces, which underpin what we call a ‘superionic state’ in metallic nanopores. It explains an ‘anomalous’ increase of the capacitance with a decrease of the pore size [6, 7]. We have also predicted an interesting voltage-induced first order transition between a cation/anion-deficient phase and a denser cation(anion)-rich phase, manifested as a jump in the capacitance. In spite of the coarse nature of the model and a number of simplifying assumptions, we believe it leads to qualitatively correct results. It would be beneficial to check its predictions using, for instance, a more robust density functional theory or Monte Carlo/molecular dynamics simulations, which can also probe the discussed effects in a wider range of pore sizes, and of course to verify them by experiments.

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