Impurities Limit the Capacitance of Carbon Based Supercapacitors

Timothy Duignan, Xiu Song Zhao

Submitted date: 29/09/2018 • Posted date: 01/10/2018
Licence: CC BY-NC-ND 4.0
Citation information: Duignan, Timothy; Zhao, Xiu Song (2018): Impurities Limit the Capacitance of Carbon Based Supercapacitors. ChemRxiv. Preprint.

Supercapacitors cannot fulfill their potential as energy storage devices without substantially improving their comparatively low energy density. This requires improving their capacitance. Unfortunately, predicting the capacitance of the carbon-based materials that typically make up supercapacitor electrodes is difficult. For example, remarkably we lack a theoretical understanding of the capacitance of even the most basic example of a carbon electrode: highly oriented pyrolytic graphite (HOPG). This material has a capacitance that is an order of magnitude lower than both standard metals and theoretical expectations. Here, we use new quantum mechanical calculations in combination with a critical analysis of the literature to demonstrate that the standard explanations of this unusually low capacitance are inadequate. We then demonstrate that a layer of hydrocarbon impurities which has recently been shown to form on graphite is the most plausible explanation. We develop a model of this effect which accounts for the penetration of solvent into the hydrocarbon layer as the voltage increases. This model explains the characteristic V shape of the capacitance as a function of voltage. Finally, we present evidence that this layer also forms and limits the capacitance in real supercapacitor materials such as activated carbon. Methods of modifying or removing this layer could therefore potentially lead to significant improvements in the capacitance of typical supercapacitors.

File list (1)

graphitecapacitance.pdf (1.59 MiB)
Impurities limit the capacitance of carbon based supercapacitors.

Timothy T. Duignan* and Xiu Song Zhao*

School of Chemical Engineering, The University of Queensland, St Lucia, Brisbane 4072, Australia

E-mail: t.duignan@uq.edu.au; george.zhao@uq.edu.au
Abstract

Supercapacitors cannot fulfill their potential as energy storage devices without substantially improving their comparatively low energy density. This requires improving their capacitance. Unfortunately, predicting the capacitance of the carbon-based materials that typically make up supercapacitor electrodes is difficult. For example, remarkably we lack a theoretical understanding of the capacitance of even the most basic example of a carbon electrode: highly oriented pyrolytic graphite (HOPG). This material has a capacitance that is an order of magnitude lower than both standard metals and theoretical expectations. Here, we use new quantum mechanical calculations in combination with a critical analysis of the literature to demonstrate that the standard explanations of this unusually low capacitance are inadequate. We then demonstrate that a layer of hydrocarbon impurities which has recently been shown to form on graphite is the most plausible explanation. We develop a model of this effect which accounts for the penetration of solvent into the hydrocarbon layer as the voltage increases. This model explains the characteristic V shape of the capacitance as a function of voltage. Finally, we present evidence that this layer also forms and limits the capacitance in real supercapacitor materials such as activated carbon. Methods of modifying or removing this layer could therefore potentially lead to significant improvements in the capacitance of typical supercapacitors.

Introduction

The development of improved supercapacitors or electric double layer capacitors (EDLCs) is an important scientific challenge. These devices can be rapidly charged, have long-life times and can be made from environmentally friendly, abundant and low cost materials. This makes them perfectly suited to serve as the next generation of energy storage devices. EDLCs are particularly useful when paired with a battery type electrode to form hybrid devices, such as sodium ion capacitors.
Carbon based materials such as activated carbon are overwhelmingly the most common choice for EDLC electrodes due to their low cost, large surface area and good electronic conductivity. A large body of literature has focussed to developing methods of making new carbon materials to serve as electrodes for EDLCs.\textsuperscript{10–19}

A key limitation of these electrodes, particularly when paired with battery electrodes in hybrid devices, is their relatively low energy density. A key way to improve their energy density is to increase the capacitance because the energy stored is given by \( E = \frac{1}{2} CV^2 \) where \( C = \frac{Q}{V} \). In order to rationally improve the capacitance of these devices it is necessary to have a fundamental understanding of what determines the capacitance based on quantitatively predictive theoretical models. Building these models for complex carbon surfaces such as activated carbon is not possible if we first cannot understand the capacitance of the simplest example of a carbon electrode, which is highly oriented pyrolytic graphite (HOPG). HOPG is essentially atomically smooth pure graphite. Unfortunately, we still lack an understanding of the capacitance of this material and therefore cannot claim to properly understand the capacitance of any carbon based materials. This lack of understanding is particularly problematic as there is good evidence, that we lay out below, that the factors limiting the capacitance of HOPG are also important for real carbon based electrode materials for supercapacitors such as activated carbon. Remarkably this lack of basic understanding goes almost entirely unremarked upon in the large literature reviewing the use of carbon based materials as EDLC electrodes.

As Figure 1 shows the capacitance of HOPG is more than an order of magnitude lower than the capacitance of normal metals such as silver and shows qualitatively different behaviour. The source of this large discrepancy has been the source of ongoing discussion for decades which continues to this day.\textsuperscript{22,23} The most common approach to understand the capacitance of EDLCs is to model or simulate the distribution of ions in the electrolyte, i.e., the electric double layer (EDL). The capacitance associated with the EDL can be adequately modelled by the solution to the Poisson-Boltzmann (PB) equation with appropriate mod-
Figure 1: The capacitance of HOPG in NaF aqueous electrolyte compared with silver in NaF and KPF$_6$ aqueous electrolyte showing that there is an order of magnitude difference and qualitatively different behaviour.
ifications such as finite size effects and surface binding. This is excellently demonstrated by Uematsu et al.\textsuperscript{23} who show that the capacitance of silver in aqueous electrolyte is well reproduced using a numerical solution of the PB equation with only a few fitted parameters of plausible size. However, the dramatic difference in the capacitance of HOPG compared with metals cannot be explained in terms of the EDL alone. There is no way to reproduce such low capacitance values with solutions of the PB equation and reasonable parameters. There will be modest differences in ion surface interactions for silver compared with HOPG but this cannot explain the large discrepancy. This has been shown theoretically by Uematsu et al.\textsuperscript{24} who demonstrate that including even large ion adsorption energies has only modest effects on the capacitance at moderate salt concentrations. Additionally, Figure 1 shows the capacitance of two different salts with a silver electrode. Although there is a substantial difference at positive potentials which is likely caused by fluoride-silver charge transfer interactions this effect is qualitatively very different from the behaviour observed on graphite with sodium fluoride electrolyte. Some other factor that limits the capacitance must therefore be at work.

Most likely this additional factor is a dielectric dead layer.\textsuperscript{25} This is a layer of very low dielectric constant in between the surface charge on the electrode and the high dielectric electrolyte solution and is depicted in Figure 2. Such a dielectric dead layer has been employed to explain anomalously low capacitance of normal capacitors.\textsuperscript{25} This layer will contain a large change in the electrostatic potential causing a low capacitance. The capacitance of a dead layer of material characterised by a width $d$, area $A$ and dielectric function $\epsilon_i$ is given by:

$$C_{DL} = \frac{\epsilon_0 \epsilon_i A}{d}$$

where DL stands for dead layer, distinct from the electric double layer (EDL). To have remained unidentified for so long this layer must be very thin and therefore must have a very low dielectric constant. It is crucially important to identify the origin of this dielectric dead layer. This is because the inverse additive nature of capacitance means that the dead
Figure 2: A depiction of the dielectric dead layer (brown), the parameters characterising it, and the different types of capacitance discussed in this article.
layer will limit the total capacitance of the device. For example, we can determine a rough estimate of 3 $\mu$F cm$^{-2}$ for the total capacitance of graphite$^{20}$ and 40 $\mu$F cm$^{-2}$ for the EDL capacitance which is approximately the capacitance measured on silver$^{21}$ (this combines the Helmholtz and diffuse layer capacitance). We can then use these values in combination with the equation for combining capacitances in series $\frac{1}{C_{\text{tot}}} = \frac{1}{C_{\text{EDL}}} + \frac{1}{C_{\text{DL}}}$ to determine a dead layer capacitance of 3.24 $\mu$F cm$^{-2}$. This means that even if the EDL capacitance was increased to infinity the total capacitance would barely increase at all as it would be limited by the dead layer. This implies that changes in the structure of the EDL will have little effect on the capacitance of the system. This indicates that modelling and understanding the behaviour of the EDL is of limited utility while the origin of this dielectric dead layer is still unknown.

There are two main explanations for this dielectric dead layer that have been put forward. The first is the so called space charge capacitance. This corresponds to a very low dielectric constant in between where the charge resides on the electrode surface (given by an effective position of surface charge: $z_\sigma$) and where the metal surface ends. This $z_\sigma$ is believed to be further inside a graphite surface than for a metal surface. A second explanation is that the dielectric function of water on the surface of graphite is reduced. This could be a result of a suppressed ability of the water molecules to orient perpendicular to the graphite surface. The effective position at which the bulk dielectric behaviour is begins can be characterised by the parameter $z_\epsilon$. The definition of the parameters characterising the dielectric dead layer are also shown in Figure 2.

These two effects could both contribute and the total size of the dielectric dead layer is given by: $z_\epsilon - z_\sigma$. Given the estimate of 3 $\mu$F cm$^{-2}$ for the capacitance of the dielectric dead layer determined above and assuming a dielectric function of 1, which corresponds to the dielectric constant of vacuum, we can use Eq. 1 to arrive at an estimate of $z_\epsilon - z_\sigma = 3$ Å for the width of the dielectric dead layer, which is very small. It is therefore important that these parameters be very accurately determined. In this article we will carefully examine the evidence for the size of these parameters using new calculations and comparing with results
in the literature where available. We demonstrate that both of these effects combined are of not sufficient to explain the low capacitance of HOPG.

Having ruled out these explanations we turn to a third possible explanation for this dielectric dead layer, which is is that it consists of adsorbed impurities, likely hydrocarbons. We outline the emerging evidence that this mechanism can quantitatively explain the dielectric dead layer and provide a model of this effect to interpret the capacitance of carbon materials as a function of potential.

Theory

Figure 2 implies that the charge on the electrode and in the electrolyte are located at specific positions. Obviously in reality there will be a more complex charge distribution as a function of $z$. However, from the Poisson equation in 1 dimension it can be seen that these two cases are actually equivalent if we are only interested in the electrostatic potential outside of the region where the charge resides. A charge density ($\rho(z)$) will create a constant electric field, i.e, a linearly varying electrostatic potential. The size of the electric field (the slope of the potential) will be determined by the total surface charge density ($\sigma = \int dz \rho(z)$) The effective location of this surface charge is determined by a weighted average:

$$z_\sigma = \frac{\int dz z \rho(z)}{\sigma}$$

Equivalently, this position can be determined by extrapolating the linear electrostatic potential to the point where it intercepts with the constant potential inside the material. The capacitance can then be calculated using the standard equation for the capacitance of a parallel plate capacitor where the effective positions $z_e - z_\sigma$ is used to determine the separation.
The CP2K simulation suite (http://www.cp2k.org) was used with the quickstep algorithm for the DFT calculations. Shorter range double zeta basis sets were used in conjunction with GTH pseudopotentials and a 400 Ry cutoff for the auxiliary plane wave basis. The Perdew, Burke, and Ernzerhof (PBE) functional was used. Wavelet 2D boundary conditions were used. The graphite was in a ABABAB structure with 200 carbon atoms per layer. The structures were taken from American Mineralogist Crystal Structure Database. The cell parameters were 24.64×30×24.64 Å. Calculations were performed on the basal plane. Calculations on silver were performed on the 100 face with cell dimensions of 14.3017×40×14.3017 Å containing 172 atoms. Surface charge was added by increasing charge parameter in CP2K. The electrostatic potential was output and subtracted from the potential for the neutral case. The origin of the $z$ axis is defined to be the position of the top most layer of atoms. The low charge density used for both graphite and graphene is 6.09 $\mu$ C cm$^{-2}$ the high charge density is 18.28 $\mu$ C cm$^{-2}$. The charge density used for silver is 15.67 $\mu$ C cm$^{-2}$.

Figure 3: Graphite structure used in quantum calculations
Results and Discussion

Space Charge layer

The most likely widely discussed candidate for the dielectric dead layer is referred to as the space charge capacitance,\textsuperscript{22} it is sometimes also referred to as the metal capacitance.\textsuperscript{33} Essentially this explanation assumes that the $z_\sigma$ parameter is negative so that the charge lies inside the graphite below the top carbon layer of graphite. This contrasts with silver where this parameter is positive, i.e., above the top layer of silver atoms. The physical reason for this is that carbon has a smaller electronic density of states compared with standard metals and is therefore not a perfect conductor and excess charge will not reside in a sharp layer on the surface of the metal but will be distributed somewhat deeper into the carbon surface. This was the original explanation proposed by Gerischer,\textsuperscript{22} where an estimate of the density of states was used to estimate this contribution. Direct quantum chemical calculation is preferable to using these simpler models however as they rely on several assumptions. Luque and Schmickler\textsuperscript{33} use quantum chemical calculations of silver and graphite surfaces in an electric field to compute this parameter to be $z_\sigma = 0.5$ Å and $z_\sigma = -1.5$ Å for silver and graphite respectively. There are several issues with these calculations however. Firstly, a surface polarised by an external electric field will not necessarily be equivalent to one where the electrons are added or removed from the surface. Secondly, Uematsu et al.\textsuperscript{23} have shown that the dielectric dead layer can be ignored for the capacitance of silver. However, as we will see below $z_\sigma$ must be at least 1 Å for the dielectric dead layer to be negligible. These problems are partly overcome by Zhan and Jiang\textsuperscript{34} who combine an implicit solvent model and a quantum mechanical treatment of the electrode using the Joint-density functional. This allows for calculations of the electric potential created by charged graphite layers. However, it is not clear how to relate the dielectric and quantum capacitances they determine to the more widely understood space charge capacitance. For example, no estimates of the $z_\sigma$ value for these materials is provided meaning comparison with other work is difficult.
Additionally, the predicted capacitances of graphite at the point of zero charge (PZC) are too large in comparison with experiment,\textsuperscript{35} whereas the capacitance of graphene away from the PZC is too small. It also appears that the implicit solvent model has a value for $z_\varepsilon$ that is inconsistent with molecular dynamics simulation as will be discussed below. More work is therefore needed to understand the capacitance of graphite and graphene.

Here, we compute this $z_\sigma$ value directly from quantum chemical calculations by creating a net charged system. The main challenge in doing this is that Ewald periodic boundary conditions normally used in these cases are not suited to studying charged 2D systems. This is because artefacts associated with the neutralising background charge arise. A better method of resolving this problem is to use boundary conditions specifically designed for charged systems with 2D periodicity. This is possible using the method developed by Genovese et al.\textsuperscript{30,31} for this purpose that has been implemented in CP2K. Applying this method to a slab of silver and a slab of graphite with a surface charge is shown in Figure 4. It is

![Graph showing electrostatic potential](image)

**Figure 4:** Electrostatic potential created by a charged silver surface and a charged graphite surface showing $z_\sigma$ is only somewhat smaller for graphite.
immediately clear that there is no evidence for the $z_\sigma = -3.2$ Å parameter required to fit the capacitance of HOPG.\textsuperscript{23} Instead graphite is characterised by a value of $z_\sigma = +0.5$ Å. However, $z_\sigma$ is 1 Å larger for the silver electrode, this indicates that perhaps graphite will have a maximum capacitance that is somewhat lower compared with silver. For silver we know the dielectric layer can be neglected which implies $\varepsilon - z_\sigma < 0$. The position of the silver charge layer is $z_\sigma = 1.3$Å which as we will discuss below is large enough to remove the dielectric dead layer.

Experiments demonstrate the capacitance of graphite increases quite substantially as the number of layers is reduced.\textsuperscript{35} To explore this effect we have computed the electrostatic potential on a single graphene layer as well as the six layer graphite given above. Figure 5 shows there is very little difference between these two cases indicating that changes in the $z_\sigma$ parameter do not explain the variation as a function of layer number.

![Figure 5: Electrostatic potential created by charged graphene and six layer graphite surfaces showing negligible differences.](image)

It is useful to examine whether this $z_\sigma$ varies with surface charge. It is known that
the capacitance of graphite shows a V shape as a function of potential.\textsuperscript{20} This V shape is accentuated for graphene.\textsuperscript{35} This implies that the $z_\sigma$ should vary as a function of surface charge if it is the cause of the low capacitance. Figure 6 shows that it does not, barely varying at all for both graphene and graphite as a function of surface charge indicating again that this is not the source of the low capacitance of graphite.

![Figure 6](image)

Figure 6: Electrostatic potential of graphite and graphene for low and high surface charges as a function of distance from the top layer showing no variation in $z_\sigma$ parameter.

**Quantum Capacitance**

There is an additional possible cause of the low capacitance that is not related to a dead layer. It is called the quantum capacitance,\textsuperscript{36,37} It is believed to become more important for graphene due to its 2D nature. It is related to the electronic density of states,\textsuperscript{36} although it is distinct from the so called space charge capacitance, which is also related to the density of states.\textsuperscript{38} There is currently no consensus on how to reliably calculate the quantum capacitance. For example, this quantity has been calculated for single and multi layer graphene by Fang et al.\textsuperscript{37} (Fig 4.), Zhan and Jiang\textsuperscript{34} (Fig 4.), Radin et al.\textsuperscript{39} (Fig. 2), Ji et al.\textsuperscript{35} (Fig. 4b), Zhan et al.\textsuperscript{40} (Fig. 1), Vatamanu et al.\textsuperscript{41} (Fig. 1) and Wood et al.\textsuperscript{42} (Fig. 1). All of these calculations differ, in some cases quite substantially, but none show a low enough
capacitance for multi layer graphene to explain the low capacitance of HOPG, although it could potentially make a non-negligible contribution in some cases. It is not possible to determine the size of this contribution until more reliable methods for determining it are established. Empirically the capacitance of graphene is observed to be similar to graphite at the PZC and larger than graphite away from the PZC.\textsuperscript{35} This indicates that if this effect is significant for graphene there must be a cancellation of different contributions.

Dead water layer

If the $z_\sigma$ parameter cannot explain the low capacitance perhaps it can be explained by the $z_\epsilon$ parameter. In other words perhaps there is a dielectric dead layer of solvent at the surface of graphite. This dead solvent layer might appear for graphite silver due to the difference in hydrophilicity. This possibility has been extensively explored by Bonthuis et al.\textsuperscript{43} who determine the $z_\epsilon$ parameter for a standard water model in contact with both hydrophilic and hydrophobic surfaces. In reality there are large fluctuations in the dielectric constant as a function of distance but an effective measure of the $z_\epsilon$ parameter can be determined. They refer to it as $z_{\text{DDS}}$ and determine a value of 1 Å for hydrophilic surface and 1.2 Å for a hydrophobic surface. Combining these values with the 0.5 Å determined above for $z_\sigma$ of graphite we arrive at a capacitance of 13-18 µFcm$^{-2}$ using a dielectric constant of 1 for the dielectric dead layer which is much larger than is experimentally observed and demonstrates that even these two effects combined cannot explain the low capacitance. This value of 1-1.2 Å should be confirmed by simulation with different water models, but it seems unlikely that this value will change much as water models tend to be fairly consistent and agree fairly well with experiment when calculating the properties of surfaces.\textsuperscript{44,45}

It has recently been proposed by Fumagalli et al.\textsuperscript{46} that there are two to three layers ($d = 7.5$ Å) of highly orientationally restricted water molecules on the surface of graphite and hexagonal boron nitride hBN. They argue that this layer is characterised by a very low dielectric constant ($\epsilon_i = 2.1$). This is inferred from dielectric spectroscopy measurements of
water in very small channels. This dielectric dead layer of orientationally restricted water is not presumed to be caused by the confinement of the water in nano sized channels. Instead this region is presumed to be present on all surfaces and is simply more noticeable for water confined in a small environment. Using the the parameters measured by Fumagalli et al.\textsuperscript{46} and Eq. 1 predicts a capacitance of 2.5 F cm\textsuperscript{-2}. This value is in good agreement with measurements of the capacitance of the HOPG surface in electrolyte solution at the PZC. Because both experiments exhibit the same anomalous behaviour characterised by the same parameters it is reasonable to presume that the cause of the dielectric dead layer is the same in both cases.

However, in our view there is insufficient evidence to conclusively attribute this dielectric dead layer to orientationally restricted surface water. Firstly, no evidence from electromagnetic spectroscopy has shown the presence of an orientationally restricted water layer. Dielectric spectroscopy works by measuring the spatial derivative of the capacitance and using a model to infer dielectric constants. So given that capacitance measurements have already indicated a dielectric dead layer is present on graphite, the results are not very surprising and do not necessarily conclusively demonstrate a physical cause. Secondly, the capacitance of HOPG in non-aqueous solvent is very similar to in aqueous solvent.\textsuperscript{20,38} This strongly implies the orientational dead layer is not a property of the solvent and means it cannot be attributed to the unusual hydrogen bonding structure or water. Thirdly, the capacitance of freshly exposed HOPG is known to vary quite substantially as a function of time exposed to air.\textsuperscript{47} It is very difficult to reconcile this observation with an orientationally restricted water layer which will equilibrate rapidly. Fourthly, a dielectric constant of 2.1 for water is so low that the electronic polarizability of water must be almost the only contribution. It is very difficult to see any path to reconcile such a dielectric dead layer of water with the molecular dynamics simulation of Bonthuis et al.,\textsuperscript{43} which would have to be qualitatively wrong.

The measurements of Fumagalli et al.\textsuperscript{46} do provide additional evidence that the space charge capacitance is not the explanation of the low capacitance of HOPG. This is because
the dielectric dead layer appears to form on both the graphite and the hBN surface. The hBN surface is not acting as an electrode in this experiment and so this cannot be explained in terms of a space charge layer as there is no charge on the electrode.

**Surface contamination**

**Experimental evidence**

If the standard explanations of the dielectric dead layer are insufficient, what could the cause be? There is a growing and compelling body of experimental evidence which indicates that the effect is caused by a thin layer of impurities adsorbed to the graphite surface.\(^{47-52}\)

This research demonstrates that freshly exposed graphite has a contact angle of approximately 60° indicating a mildly hydrophilic surface in agreement with theory.\(^{48,50}\) This contact angle then rapidly increases as a function of time exposed to air increasing to roughly 95° where it can stabilise.\(^{50,51}\) The adsorption of hydrocarbon impurities is the most plausible explanation for this behaviour. Remarkably this means the value of 95° for the contact angle of water on graphite, which is almost universally observed, is not a property of true graphite.\(^{48}\)

Spectroscopy has been used to confirm the presence of hydrocarbon impurities at the surface which increase over the same time frame.\(^{52}\) The thickness of this layer has been measured by spectroscopic ellipsometry (SE) to rapidly increase and stabilise at around 5-8.5 Å.\(^{52}\) This is depicted in Figure 7 where the data is taken from Ref. 52. The areal capacitance also decreases during this time.\(^{47,52}\)

Indeed, this research shows that the 2-3 μFcm\(^{-2}\) value for the capacitance of graphite is not the maximum achievable and that by taking care to improve the cleanliness of the sample it can be increased substantially.

Another piece of evidence to support this hypothesis is that trace concentrations of surfactant impurities are essentially impossible to remove from water. The pure air-water surface displays a negative zeta potential of -300mV this has been convincingly demonstrated to be attributable to trace concentrations of negatively charged surfactant impurities adsorbing to the surface.\(^{53,54}\) Similarly, it has recently been demonstrated that the Jones-Ray effect,
which is a puzzling observation regarding the surface tension of the air-water interface, can be explained in terms trace concentration of surfactant impurities.\textsuperscript{55,56} Clearly if it is not possible to create a pristine air-water surface there is no reason to believe that these contaminants can be avoided at the graphite water surface. The power of impurities to explain puzzling surface phenomena has also very recently been demonstrated by Balajka et al.\textsuperscript{57} who show a self assembled monolayer spontaneously forms on the surface of titanium dioxide from part per billion levels of atmospheric carboxylic acids. Physically the reason that it is impossible to stop impurities accumulating at interfaces is that the surface adsorption free energy can be $-15 \ k_B T$ or more. When this value is used in the Boltzmann equation it shows that micro molar impurities in bulk is sufficient to cause molar concentrations at the surface.

A third line of evidence comes from Uematsu et al.\textsuperscript{23} who examine the capacitance of graphite at very low salt concentrations and show that it is necessary to assume a very large adsorption energy to explain the experimental capacitance. The adsorption energy of sodium and fluoride ions to graphite surfaces could not plausibly be so large. Their proposed
explanation for this is that there are charged surfactant impurities in the solution which are adsorbing at low concentrations just as in the Jones-Ray effect.

Metals are substantially more hydrophilic even than pristine graphite often with a very small contact angle. This could substantially reduce the affinity of hydrocarbon molecules for the surface enough to prevent the formation of this layer.

The dielectric dead layer observed by Fumagalli et al.\textsuperscript{46} is characterised by a thickness of $7.5 \pm 1.5$ Å and a dielectric constant of $2.1 \pm 0.2$. This thickness matches very well the measured thickness of the adsorbed hydrocarbon layer on the surface of graphite\textsuperscript{52} and a dielectric constant of 2.1 is very typical of hydrocarbons. Additionally, these authors acknowledge that these surfaces when unconfined inevitably accumulate a layer of hydrocarbon impurities on both the graphite and hBN surfaces.\textsuperscript{58} It therefore seems plausible that the dielectric dead layer is a result of hydrocarbon impurities, at least for the larger channels (20 nm) where confinement effects are unlikely to occur.

Model of HOPG capacitance.

Using rough estimates for the properties of the hydrocarbon layer of $d = 6$ Å and $\epsilon_i = 2$ we can predict a capacitance of $3 \mu F cm^{-1}$, which agrees well with experimental measurements of the capacitance at the PZC. If impurities are the cause of the low capacitance there must be some explanation of the characteristic V shaped capacitance as a function of potential in terms of the hydrocarbon layer. From the equation for the capacitance of the dead layer (Eq. 1) we can see that either the layer thickness must be decreasing with increasing potential or the surface area or the dielectric function must be increasing with potential. A decreasing thickness is not plausible because for graphene the thickness would need to be reduced by a factor of approximately five\textsuperscript{35} which is too small for any plausible hydrocarbon layer. An increase in surface area is unlikely as the capacitance is measured using impedance spectroscopy and the equilibration time of the desorption of the hydrocarbon layer will be too slow to be observed at the frequencies used. An increase in the dielectric function on the other hand can be
explained in terms of water molecules being absorbed by the layer of hydrocarbons as the electric field in the hydrocarbon layer increases along with the potential. This will favour the transfer of water molecules from bulk into this layer which will increase the dielectric constant and hence increase the capacitance. To model this effect quantitatively we assume the density of water in the hydrocarbon layer is given by the Boltzmann equation:

\[ \rho_{\text{solv}}^{\text{surf}} = \rho_{\text{solv}}^{\text{bulk}} \exp^{-\beta G_{\text{surf}}} \] (3)

We can calculate the energy gain on transferring a water molecule into the hydrocarbon layer from a constant transfer free energy at the PZC plus the energy of inserting a dipole in an electric field. \( G_{\text{surf}} = G_{\text{pzc}} - \mu E \) where \( \mu \) is the dipole moment of a solvent molecule and \( E = V/d \) is used for the electric field, where \( d \) is the thickness of the hydrocarbon layer. This provides an estimate of the density of water molecules in the hydrocarbon layer which can then be used to estimate the dielectric constant of the hydrocarbon layer with the using a linear interpolation between the dielectric function of pure hydrocarbon and pure water:

\[ \epsilon_i = \epsilon_{\text{HC}} + \frac{\rho_{\text{solv}}^{\text{surf}}}{\rho_{\text{solv}}^{\text{bulk}}} \epsilon_{\text{solv}} \] (4)

The differential capacitance is then given by \( \frac{d\sigma}{dV} \) where \( \sigma = \frac{\epsilon \epsilon_0 V}{d} \). Combining these equations we arrive at the following expression for the capacitance as a function of voltage:

\[ C_{\text{diff}} = \frac{\epsilon_0}{d} \exp^{-\beta G_{\text{pzc}}} \left( \epsilon_{\text{HC}} \exp^{\beta G_{\text{pzc}}} + \epsilon_{\text{solv}} \left(1 + \frac{\beta \mu V}{d}\right) \exp^{\beta \mu V/d}\right) \] (5)

We neglect the contribution to the capacitance from the \( \approx 0.5 \) Å thick dielectric dead layer associated with the \( z_\epsilon - z_\sigma \) parameter. This term only makes a small contribution, which does not qualitatively change the conclusions. There are five parameters in this expression which means there is significant risk of over fitting. However tight bounds on all of these parameters can be provided significantly limiting this risk. Firstly \( G_{\text{pzc}} \) must be less than
the solvation energy of a solvent molecule itself, which is 25 kJ mol\(^{-1}\) for water\(^{59}\) and similar for acetonitrile.\(^{60}\) This is because there will be a favourable dispersion interaction of the solvent with the hydrocarbon molecules which will reduce the penalty of desolvating it. \(\epsilon_{\text{solv}}\) for water is known to be 78 and 40 for acetonitrile. \(\epsilon_{\text{HC}}\) should be close to 2 as that is the dielectric constant of most oils. \(d\) should be 5 - 8.5 Å\(^{52}\) and finally \(\mu\) should be of the order of the dipole moment of the solvent molecules, ie 1 - 3 Debye. However, it cannot be expected to be precisely the same as the gas phase value as there will be many body polarisation effects and higher order multipole effects which will give it a different effective value in solution. For instance water’s dipole moment is known to be substantially higher in bulk water than in vacuum. For acetonitrile we allow for a dipole moment that depends on the sign of the potential. This is necessary due to the fact that there are higher order multipole moment contributions which will create a potential asymmetry and are implicitly incorporated into the dipole term.

![Figure 8: Capacitance of HOPG in water and acetonitrile in comparison with the model.](image)

By fitting Eq. 5 to various experimental measurements of the capacitance the experimental values of can be well reproduced for single and multilayer graphite in both aqueous and non-aqueous solvent. This is shown for HOPG in water and acetonitrile in Figure 8. Table 1 gives the parameters determined by fitting, showing that they fit within the plausible ranges. The only surprise is that the fitted dipole moment of acetonitrile is approximately half that for the water the dipole moment of acetonitrile in vacuum is actually roughly twice
Table 1: Parameter values

| Capacitor                          | $U_{\text{transfer}}$ (kJmol$^{-1}$) | $\epsilon_{\text{HC}}$ | $\epsilon_{\text{solvent}}$ | $\mu_+$ (D) | $\mu_-$ (D) | $d$ Å |
|------------------------------------|--------------------------------------|-------------------------|-----------------------------|-------------|-------------|-------|
| Estimated range                    | 10-20                                | 2                       | 40/78                       | 1-5         | 1-5         | 5-10  |
| HOPG water$^{20}$                  | 17                                   | 2                       | 78                          | 2.4         | 2.4         | 6.3   |
| Graphene aqueous$^{35}$            | 10.5                                 | 2                       | 78                          | 2.4         | 2.4         | 11    |
| 5 layer graphene aqueous$^{35}$    | 15                                   | 2                       | 78                          | 2.4         | 2.4         | 11    |
| HOPG acetonitrile$^{38}$           | 15                                   | 2                       | 40                          | 1.1         | 1.4         | 6.4   |
| Activated Carbon acetonitrile$^{61}$| 15                                   | 2                       | 40                          | 1.1         | 1.4         | 3.1   |

that of water in vacuum. However, the dielectric function of acetonitrile is close to half that of water, which is perhaps a better indicator of this molecules effective dipole moment in solution.

It is also worth noting that there is a non trivial amount of variation in the experimentally measured values for the capacitance as shown by Zou et al.$^{47}$ who showed that the capacitance can be substantially larger and that it decreases as a function of exposure time to air. This is again consistent with the cause being attributable to hydrocarbon impurities and means that some parameters are necessary to model this effect until the properties of this hydrocarbon layer are more accurately determined.

![Figure 9: Capacitance of single layer graphene five layer graphene in water in comparison with the model.](image)

Figure 9: Capacitance of single layer graphene five layer graphene in water in comparison with the model.

In addition the sharper V shape of graphene in comparison with graphite can also be reproduced by using different values for the parameters as is shown in Figure 9. The parameters are given in Table 1. It is clear that the capacitance as a function of layers can be explained
by the hydrocarbon layer becoming larger but more penetrable by water molecules. This is reasonable considering that it is known from contact angle measurements that graphene demonstrates partial wetting transparency.\textsuperscript{62} This means that the hydrophilicity of graphene can be quite different to graphite depending on the substrate. This difference in hydrophilicity will result in differences in the structure and nature of the adsorbed hydrocarbon layer formed on the surface of the carbon which could plausibly lead to a less diffuse hydrocarbon layer.

**Real EDLC electrodes**

The capacitances of more complex carbon materials such as activated carbon and carbide derived carbons with neutral electrolytes are only somewhat larger per unit of surface area than HOPG, i.e., 6-10\(\mu\text{Fcm}^{-2}\).\textsuperscript{61} It is therefore quite likely that the same limiting factor is playing a role for these materials. Additionally, these materials show the same V shape characteristic capacitance as a function of surface charge indicating the same dead layer is present. Figure 10 shows a fit of the above model to the experimentally measured capacitance of real EDLC electrode material: activated carbon in acetonitrile. The fit is reasonably good. Most importantly, the parameters used are almost the same as the ones used to describe capacitance of HOPG in acetonitrile. The only difference is a thinner layer of hydrocarbons is used. This could plausibly be a result of the curved porous nature of the activated carbon, which could impair the ability of the hydrocarbons to form an even adsorbed layer. Interestingly the activated carbon and HOPG in acetonitrile both display the same potential asymmetry. With the capacitance for positive potentials being larger than for negative potentials by approximately the same amount. This again indicates that the mechanism limiting the capacitance is the same for both activated carbon and HOPG. This consistency highlights the usefulness of developing an understanding of the capacitance of HOPG before attempting to model more complex surfaces such as activated carbon.

One obvious way to test the hypothesis that hydrocarbon impurities reduce the capacit-
Figure 10: Comparison of capacitance model with measurements on a real EDLC electrode: activated carbon in acetonitrile as measured by Hahn et al.\textsuperscript{61}
tance of activated carbon is to deliberately add surfactant to solution and look at the effect on the capacitance. If the system is uncontaminated to begin with there should be a significant decrease in the areal capacitance of the system as the surfactant will adsorb to the surface and reduce the available surface area. If the surfaces are already saturated with organic impurities there should be minimal chance in the capacitance. This experiment has in fact already been carried out on activated carbon and shows that adding surfactant to activated carbon based electrodes barely affects the capacitance at all. The most plausible explanation for this is that there are already hydrocarbon contaminants adsorbed to the surface preventing the surfactant from adsorbing.

Various factors are known to alter the capacitance of activated carbon. These alterations are commonly attributed to changes in the behaviour of the EDL. A large amount of research has therefore focused on simulating the behaviour of the EDL near complex activated carbon based electrodes. However, if the behaviour of the EDL is not the dominant factor limiting the capacitance then the it is not clear that this approach will offer useful insights for how to further improve the capacitance. Rather, a focus should be on understanding the nature of this hydrocarbon layer and developing new approaches to prevent and control its formation. For example, perhaps this layer can be replaced with conductive polymer if it is added before this hydrocarbon layer can form.

A good example of this is the well known ‘anomalous’ enhancement of the capacitance of nano-porous carbon. Understanding the physical origin of this enhanced capacitance has attracted significant attention in recent years. In some sense this problem has been framed the wrong way around. What is anomalous is the low capacitance of HOPG and normal activated carbon in comparison with standard metals. The challenge is therefore to explain why nano-porous activated carbon does not show this anomalously low capacitance. Most common explanations of this enhancement refer to the distribution of ions in the solution phase and phenomena such as over-screening and ion dehydration. However these are all properties of the EDL, and changing the properties of the EDL will not improve
the capacitance if a dielectric dead layer is the main factor limiting the capacitance. Evidence that the nano-porous capacitance enhancement is not caused by the behaviour of the EDL is that a similar enhancement occurs at the same length scale for 6M aqueous KOH, 1 M aqueous HSO4, 1 M TEABF4 in acetonitrile and ionic liquid which are very different.\textsuperscript{66,73}

If a dielectric dead layer does limit the capacitance of activated carbon then the cause of the enhanced capacitance in nano-porous carbon must be related to changes in the properties of the dielectric dead layer. For example, a dielectric dead layer caused by adsorbed hydrocarbon impurities would be unlikely to form in sub nanometre sized pores as these molecules are generally too large to fit into nanometre sized pores. Additionally, the enhanced capacitance of nitrogen doped carbon and roughened carbon may be due to the fact that these surfaces will inhibit the formation of a thick layer of hydrocarbon impurities.

**Conclusion**

We have argued against the space charge capacitance and the orientationally dead water layer as explanations of the anomalously low capacitance of HOPG and shown that this effect is most likely caused by a layer of adsorbed hydrocarbon impurities known to adsorb on this surface. We have developed a simple model to demonstrate that this mechanism can plausibly explain the V shaped capacitance observed experimentally. We have also demonstrated that this dead layer is likely to be forming on the surfaces of carbon electrodes used in real EDLC type devices and is therefore likely to be a major limitation on the capacitance of these devices. This has important implications for how to improve the capacitance of carbon based electrodes of EDLCs such as activated carbon. In particular, it implies the detailed understanding of the distribution of ions in porous carbon electrodes will be of limited value for improving capacitance in real devices and that more attention should be focussed on surface modifications, treatments, and preparation methods that can prevent or replace this hydrocarbon layer.
Acknowledgements

XSZ and TTD acknowledge the Australian Research Council (ARC) funding via project number FL170100101 and the Research Computing Centre at UQ for providing computational resources.

References

(1) Zhang, J.; Zhao, X. S. On the configuration of supercapacitors for maximizing electrochemical performance. *ChemSusChem* **2012**, *5*, 818–841.

(2) Yan, J.; Wang, Q.; Wei, T.; Fan, Z. Recent advances in design and fabrication of electrochemical supercapacitors with high energy densities. *Adv. Energy Mater.* **2014**, *4*.

(3) Wang, Y.; Song, Y.; Xia, Y. Electrochemical capacitors: mechanism, materials, systems, characterization and applications. *Chem. Soc. Rev.* **2016**, *45*, 5925–5950.

(4) Wang, F.; Wu, X.; Yuan, X.; Liu, Z.; Zhang, Y.; Fu, L.; Zhu, Y.; Zhou, Q.; Wu, Y.; Huang, W. Latest advances in supercapacitors: From new electrode materials to novel device designs. *Chem. Soc. Rev.* **2017**, *46*, 6816–6854.

(5) Wu, Z.; Li, L.; Yan, J. M.; Zhang, X. B. Materials Design and System Construction for Conventional and New-Concept Supercapacitors. *Adv. Sci.* **2017**, *4*.

(6) Zhang, L.; Hu, X.; Wang, Z.; Sun, F.; Dorrell, D. G. A review of supercapacitor modeling, estimation, and applications: A control/management perspective. *Renew. Sustain. Energy Rev.* **2018**, *81*, 1868–1878.

(7) Zuo, W.; Li, R.; Zhou, C.; Li, Y.; Xia, J.; Liu, J. Battery-Supercapacitor Hybrid Devices: Recent Progress and Future Prospects. *Adv. Sci.* **2017**, *4*, 1–21.
(8) Aravindan, V.; Ulaganathan, M.; Madhavi, S. Research progress in Na-ion capacitors. *J. Mater. Chem. A* **2016**, *4*, 7538–7548.

(9) Wang, H.; Zhu, C.; Chao, D.; Yan, Q.; Fan, H. J. Nonaqueous Hybrid Lithium-Ion and Sodium-Ion Capacitors. *Adv. Mater.* **2017**, *29*, 1–18.

(10) Simon, P.; Burke, A. Nanostructured carbons: Double-layer capacitance and more. *Electrochem. Soc. Interface* **2008**, *17*, 38–43.

(11) Zhang, L. L.; Zhao, X. S. Carbon-based materials as supercapacitor electrodes. *Chem. Soc. Rev.* **2009**, *38*, 2520.

(12) Zhang, L. L.; Zhou, R.; Zhao, X. S. Graphene-based materials as supercapacitor electrodes. *J. Mater. Chem.* **2010**, *20*, 5983.

(13) Frackowiak, E.; Abbas, Q.; Béguin, F. Carbon/carbon supercapacitors. *J. Energy Chem.* **2013**, *22*, 226–240.

(14) Gu, W.; Yushin, G. Review of nanostructured carbon materials for electrochemical capacitor applications: Advantages and limitations of activated carbon, carbide-derived carbon, zeolite-templated carbon, carbon aerogels, carbon nanotubes, onion-like carbon, and graphene. *Wiley Interdiscip. Rev. Energy Environ.* **2014**, *3*, 424–473.

(15) Zhang, X.; Zhang, H.; Li, C.; Wang, K.; Sun, X.; Ma, Y. Recent advances in porous graphene materials for supercapacitor applications. *RSC Adv.* **2014**, *4*, 45862–45884.

(16) Choi, H.; Yoon, H. Nanostructured Electrode Materials for Electrochemical Capacitor Applications. *Nanomaterials* **2015**, *5*, 906–936.

(17) Ke, Q.; Wang, J. Graphene-based materials for supercapacitor electrodes A review. *J. Mater.* **2016**, *2*, 37–54.

(18) Chen, X.; Paul, R.; Dai, L. Carbon-based supercapacitors for efficient energy storage. *Natl. Sci. Rev.* **2017**, *4*, 453–489.
(19) Borenstein, A.; Hanna, O.; Attias, R.; Luski, S.; Brousse, T.; Aurbach, D. Carbon-based composite materials for supercapacitor electrodes: a review. *J. Mater. Chem. A* **2017**, *5*, 12653–12672.

(20) Randin, J.-P.; Yeaker, E. Differential capacitance study on the basal plane of stress-annealed pyrolytic graphite. *J. Electroanal. Chem. Interfacial Electrochem.* **1972**, *36*, 257–276.

(21) Valette, G. Double layer on silver single-crystal electrodes in contact with electrolytes having anions which present a slight specific adsorption. Part I. The (110) face. *J. Electroanal. Chem.* **1981**, *122*, 285–297.

(22) Gerischer, H. An interpretation of the double layer capacity of graphite electrodes in relation to the density of states at the Fermi level. *J. Phys. Chem.* **1985**, *89*, 4249–4251.

(23) Uematsu, Y.; Netz, R. R.; Bonthuis, D. J. Analytical interfacial layer model for the capacitance and electrokinetics of charged aqueous interfaces. *Langmuir* **2018**, *acs.langmuir.7b04171*.

(24) Uematsu, Y.; Netz, R. R.; Bonthuis, D. J. The effects of ion adsorption on the potential of zero charge and the differential capacitance of charged aqueous interfaces. *J. Phys. Condens. Matter* **2018**, *30*, 064002.

(25) Stengel, M.; Spaldin, N. A. Origin of the dielectric dead layer in nanoscale capacitors. *Nature* **2006**, *443*, 679–682.

(26) VandeVondele, J.; Krack, M.; Mohamed, F.; Parrinello, M.; Chassaing, T.; Hutter, J. Quickstep: Fast and Accurate Density Functional Calculations using a Mixed Gaussian and Plane Waves Approach. *Comput. Phys. Commun.* **2005**, *167*, 103–128.

(27) VandeVondele, J.; Hutter, J. Gaussian Basis Sets for Accurate Calculations on Molecular Systems in Gas and Condensed Phases. *J. Chem. Phys.* **2007**, *127*, 114105.
(28) Goedecker, S.; Teter, M.; Hutter, J. Separable Dual-Space Gaussian Pseudopotentials. *Phys. Rev. B* **1996**, *54*, 1703–1710.

(29) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(30) Genovese, L.; Deutsch, T.; Neelov, A.; Goedecker, S.; Beylkin, G. Efficient solution of Poisson’s equation with free boundary conditions. *J. Chem. Phys.* **2006**, *125*.

(31) Genovese, L.; Deutsch, T.; Goedecker, S. Efficient and accurate three-dimensional Poisson solver for surface problems. *J. Chem. Phys.* **2007**, *127*.

(32) Downs, R. T.; Hall-Wallace, M. The American Mineralogist crystal structure database. *Am. Mineral.* **2003**, *88*, 247–250.

(33) Luque, N. B.; Schmickler, W. The electric double layer on graphite. *Electrochim. Acta* **2012**, *71*, 82–85.

(34) Zhan, C.; Jiang, D. E. Contribution of Dielectric Screening to the Total Capacitance of Few-Layer Graphene Electrodes. *J. Phys. Chem. Lett.* **2016**, *7*, 789–794.

(35) Ji, H.; Zhao, X.; Qiao, Z.; Jung, J.; Zhu, Y.; Lu, Y.; Zhang, L. L.; MacDonald, A. H.; Ruoff, R. S. Capacitance of carbon-based electrical double-layer capacitors. *Nat. Commun.* **2014**, *5*, 3317.

(36) John, D. L.; Castro, L. C.; Pulfrey, D. L. Quantum capacitance in nanoscale device modeling. *J. Appl. Phys.* **2004**, *96*, 5180–5184.

(37) Fang, T.; Konar, A.; Xing, H.; Jena, D. Carrier statistics and quantum capacitance of graphene sheets and ribbons. *Appl. Phys. Lett.* **2007**, *91*.

(38) Gerischer, H.; McIntyre, R.; Scherson, D.; Storck, W. Density of the electronic states of graphite: Derivation from differential capacitance measurements. *J. Phys. Chem.* **1987**, *91*, 1930–1935.
(39) Radin, M. D.; Ogitsu, T.; Biener, J.; Otani, M.; Wood, B. C. Capacitive charge storage at an electrified interface investigated via direct first-principles simulations. *Phys. Rev. B - Condens. Matter Mater. Phys.* **2015**, *91*, 1–7.

(40) Zhan, C.; Neal, J.; Wu, J.; Jiang, D. E. Quantum Effects on the Capacitance of Graphene-Based Electrodes. *J. Phys. Chem. C* **2015**, *119*, 22297–22303.

(41) Vatamanu, J.; Ni, X.; Liu, F.; Bedrov, D. Tailoring graphene-based electrodes from semiconducting to metallic to increase the energy density in supercapacitors. *Nanotechnology* **2015**, *26*.

(42) Wood, B. C.; Ogitsu, T.; Otani, M.; Biener, J. First-principles-inspired design strategies for graphene-based supercapacitor electrodes. *J. Phys. Chem. C* **2014**, *118*, 4–15.

(43) Bonthuis, D. J.; Gekle, S.; Netz, R. R. Profile of the static permittivity tensor of water at interfaces: Consequences for capacitance, hydration interaction and ion adsorption. *Langmuir* **2012**, *28*, 7679–7694.

(44) Galib, M.; Duignan, T. T.; Misteli, Y.; Baer, M. D.; Schenter, G. K.; Hutter, J.; Mundy, C. J. Mass Density Fluctuations in Quantum and Classical descriptions of Liquid Water. *J. Chem. Phys.* **2017**, *146*, 244501.

(45) Medders, G. R.; Paesani, F. Dissecting the Molecular Structure of the Air/Water Interface from Quantum Simulations of the Sum-Frequency Generation Spectrum. *J. Am. Chem. Soc.* **2016**, *138*, 3912–3919.

(46) Fumagalli, L.; Esfandiar, A.; Fabregas, R.; Hu, S.; Ares, P.; Janardanan, A.; Yang, Q.; Radha, B.; Taniguchi, T.; Watanabe, K. et al. Anomalously low dielectric constant of confined water. *Science* **2018**, *1342*, 1339–1342.

(47) Zou, Y.; Walton, A. S.; Kinloch, I. A.; Dryfe, R. A. Investigation of the Differential
Capacitance of Highly Ordered Pyrolytic Graphite as a Model Material of Graphene. *Langmuir* **2016**, *32*, 11448–11455.

(48) Li, Z.; Wang, Y.; Kozbial, A.; Shenoy, G.; Zhou, F.; McGinley, R.; Ireland, P.; Morganstein, B.; Kunkel, A.; Surwade, S. P. et al. Effect of airborne contaminants on the wettability of supported graphene and graphite. *Nat. Mater.* **2013**, *12*, 925–931.

(49) Kozbial, A.; Li, Z.; Sun, J.; Gong, X.; Zhou, F.; Wang, Y.; Xu, H.; Liu, H.; Li, L. Understanding the intrinsic water wettability of graphite. *Carbon* **2014**, *74*, 218–225.

(50) Mücksch, C.; Rösch, C.; Müller-Renno, C.; Ziegler, C.; Urbassek, H. M. Consequences of Hydrocarbon Contamination for Wettability and Protein Adsorption on Graphite Surfaces. *J. Phys. Chem. C* **2015**, *119*, 12496–12501.

(51) Li, Z.; Kozbial, A.; Nioradze, N.; Parobek, D.; Shenoy, G. J.; Salim, M.; Amemiya, S.; Li, L.; Liu, H. Water protects graphitic surface from airborne hydrocarbon contamination. *ACS Nano* **2016**, *10*, 349–359.

(52) Hurst, J. M.; Li, L.; Liu, H. Adventitious hydrocarbons and the graphite-water interface. *Carbon* **2018**, *134*, 464–469.

(53) Roger, K.; Cabane, B. Why are Hydrophobic/Water Interfaces Negatively Charged? *Angew. Chemie - Int. Ed.* **2012**, *51*, 5625–5628.

(54) Joly, L.; Detcheverry, F.; Biance, A.-L. Anomalous ζ Potential in Foam Films. *Phys. Rev. Lett.* **2014**, *113*, 088301.

(55) Uematsu, Y.; Bonthuis, D. J.; Netz, R. R. Charged Surface-Active Impurities At Nanomolar Concentration Induce Jones-Ray Effect. *J. Phys. Chem. Lett.* **2018**, *9*, 189–193.

(56) Duignan, T. T.; Baer, M. D.; Mundy, C. J. Surfactant Impurities Can Explain the Jones-Ray Effect. *J. Chem. Phys.* **2018**, *Accepted*, 10.26434/chemrxiv.5732976.v3.
(57) Balajka, J.; Hines, M. A.; DeBenedetti, W. J. I.; Komora, M.; Pavelec, J.; Schmid, M.; Diebold, U. High Affinity Adsorption leads to Molecularly Ordered Interfaces on TiO2 in Air and Solution. *Science* **2018**, *361*, 786–789.

(58) Radha, B.; Esfandiar, A.; Wang, F. C.; Rooney, A. P.; Gopinadhan, K.; Keerthi, A.; Mishchenko, A.; Janardanan, A.; Blake, P.; Fumagalli, L. et al. Molecular transport through capillaries made with atomic-scale precision. *Nature* **2016**, *538*, 222–225.

(59) Ben-Naim, A.; Marcus, Y. Solvation Thermodynamics of Non Ionic Solutes. *J. Chem. Phys.* **1984**, *81*, 2016–2027.

(60) Putnam, W. E.; Mceachern, D. M.; Kilpatrick, J. E. Entropy and related thermodynamic properties of acetonitrile (Methyl cyanide). *J. Chem. Phys.* **1965**, *42*, 749–755.

(61) Hahn, M.; Baertschi, M.; Barbieri, O.; Sauter, J.-C.; Kotz, R.; Gallay, R. Interfacial Capacitance and Electronic Conductance of Activated Carbon Double-Layer Electrodes. *Electrochem. Solid-State Lett.* **2004**, *7*, A33.

(62) Rafiee, J.; Mi, X.; Gullapalli, H.; Thomas, A. V.; Yavari, F.; Shi, Y.; Ajayan, P. M.; Koratkar, N. A. Wetting transparency of graphene. *Nat. Mater.* **2012**, *11*, 217–222.

(63) Fic, K.; Lota, G.; Frackowiak, E. Effect of surfactants on capacitance properties of carbon electrodes. *Electrochim. Acta* **2012**, *60*, 206–212.

(64) Burt, R.; Birkett, G.; Zhao, X. S. A review of molecular modelling of electric double layer capacitors. *Phys. Chem. Chem. Phys.* **2014**, *16*, 6519.

(65) Zhan, C.; Lian, C.; Zhang, Y.; Thompson, M. W.; Xie, Y.; Wu, J.; Kent, P. R.; Cummings, P. T.; Jiang, D. E.; Wesolowski, D. J. Computational Insights into Materials and Interfaces for Capacitive Energy Storage. *Adv. Sci.* **2017**, *4*.

(66) Raymundo-Piñero, E.; Kierzek, K.; Machnikowski, J.; Béguin, F. Relationship between
the nanoporous texture of activated carbons and their capacitance properties in different electrolytes. *Carbon* **2006**, *44*, 2498–2507.

(67) Chmiola, J.; Yushin, G.; Gogotsi, Y.; Portet, C.; Simon, P.; Taberna, P. L. Anomalous Increase in Carbon Capacitance at Pore Sizes Less Than 1 Nanometer. *Science (80-. ).* **2006**, *313*, 1760–1763.

(68) Merlet, C.; Rotenberg, B.; Madden, P. A.; Taberna, P.-L.; Simon, P.; Gogotsi, Y.; Salanne, M. On the molecular origin of supercapacitance in nanoporous carbon electrodes. *Nat. Mater.* **2012**, *11*, 306–310.

(69) Merlet, C.; Péan, C.; Rotenberg, B.; Madden, P. A.; Daffos, B.; Taberna, P. L.; Simon, P.; Salanne, M. Highly confined ions store charge more efficiently in supercapacitors. *Nat. Commun.* **2013**, *4*, 2–7.

(70) Kondrat, S.; Kornyshev, A. Superionic state in double-layer capacitors with nanoporous electrodes. *J. Phys. Condens. Matter* **2011**, *23*, 022201.

(71) Prehal, C.; Koczwara, C.; Jäckel, N.; Schreiber, A.; Burian, M.; Amenitsch, H.; Hartmann, M. A.; Presser, V.; Paris, O. Quantification of ion confinement and desolvation in nanoporous carbon supercapacitors with modelling and in situ X-ray scattering. *Nat. Energy* **2017**, *2*.

(72) Burt, R.; Breitsprecher, K.; Daffos, B.; Taberna, P. L.; Simon, P.; Birkett, G.; Zhao, X. S.; Holm, C.; Salanne, M. Capacitance of Nanoporous Carbon-Based Supercapacitors Is a Trade-Off between the Concentration and the Separability of the Ions. *J. Phys. Chem. Lett.* **2016**, *7*, 4015–4021.

(73) Largeot, C.; Portet, C.; Chmiola, J.; Taberna, P. L.; Gogotsi, Y.; Simon, P. Relation between the ion size and pore size for an electric double-layer capacitor. *J. Am. Chem. Soc.* **2008**, *130*, 2730–2731.
