

Continuous transition from double-layer to Faradaic charge storage in confined electrolytes

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The capacitance of the electrochemical interface has traditionally been separated into two distinct types: non-Faradaic electric double-layer capacitance, which involves charge induction, and Faradaic pseudocapacitance, which involves charge transfer. However, the electrochemical interface in most energy technologies is not planar but involves porous and layered materials that offer varying degrees of electrolyte confinement. We suggest that understanding electrosorption under confinement in porous and layered materials requires a more nuanced view of the capacitive mechanism than that at a planar interface. In particular, we consider the crucial role of the electrolyte confinement in these systems to reconcile different viewpoints on electrochemical capacitance. We propose that there is a continuum between double-layer capacitance and Faradaic intercalation that is dependent on the specific confinement microenvironment. We also discuss open questions regarding electrochemical capacitance in porous and layered materials and how these lead to opportunities for future energy technologies.

Electric double-layer (EDL) formation occurs at any electrode–liquid electrolyte electrochemical interface. Understanding the EDL structure and dynamics is at the centre of the energy–water research nexus because it can advance electrochemical applications that range from energy storage and conversion to ion separation, water desalination, sensing and actuation^{1,2}. At a planar polarized metal electrode, the electrolyte solvent and ions undergo adsorption based on their charge, solvation state and relative concentration with respect to the bulk electrolyte. In the initial formalism proposed by Conway³, the resulting electrochemical capacitance is separated into an EDL capacitance that involves non-specifically adsorbed ions (where charge is induced, but not transferred) and an adsorption pseudocapacitance that involves specifically adsorbed ions and protons chemically bound to the electrode.

There has been vigorous discussion in the literature about the distinction between these two capacitances^{4,5}, which includes a challenge on the utility of the concept of pseudocapacitance itself^{6,7}. It was argued that the electrochemical response of some pseudocapacitive materials could not arise from redox reactions, but instead is the consequence of EDL formation at metallicly conductive materials, or of separate surface redox and EDL processes^{6,7}. Furthermore, there are numerous interpretations of the ‘true’ meaning of pseudocapacitance with strict borders drawn around each individual storage mechanism that primarily aim to discourage researchers from mischaracterizing ‘fast’ battery materials as pseudocapacitors^{5,8}. In a recent review⁹, the current interpretations of pseudocapacitance are described in more detail.

In this Perspective, we consider the crucial role of confinement to present a unified view of electrochemical capacitance at non-ideal interfaces. The electrochemical interface in most technological applications is not planar, but involves porous or layered

materials that offer varying degrees of electrolyte confinement (Fig. 1). Understanding of electrosorption in such materials requires a more refined view of the capacitive mechanism. The purpose of this Perspective is to provide an overview of the current understanding and discuss open questions regarding electrochemical capacitance, and charge storage in general, in porous and layered materials. We also propose a concept to reconcile different viewpoints on electrochemical capacitance by considering the continuum between double-layer capacitance and Faradaic intercalation under confinement. Rather than to strictly delimit each storage mechanism, we hypothesize that there can be a seamless transition based on the increased charge transfer between an electrolyte ion and host associated with the extent of ion desolvation and confinement. We first consider the electrochemical interface from electrosorption at a two-dimensional (2D) planar surface to electrosorption at 3D porous carbon electrodes with a continuous reduction in pore size in a step-by-step manner of increasing complexity. Then, we draw a parallel to porous or layered materials traditionally considered to undergo complete charge transfer with the intercalated ions (associated with, for example, a measurable change in the valence of a transition metal). We show that in these materials, partial solvation or the presence of solvent in the interlayer space can reduce the interaction of intercalated ion and host and thereby cause a phenomenon comparable to specific electrosorption or intercalation pseudocapacitance.

Electric double-layer at planar electrochemical interfaces

We first review ion adsorption at planar electrochemical interfaces, as this forms the foundation of our understanding of electrochemical adsorption phenomena. The nature of ion solvation at a planar electrochemical interface (Fig. 1a) determines how the ion interacts

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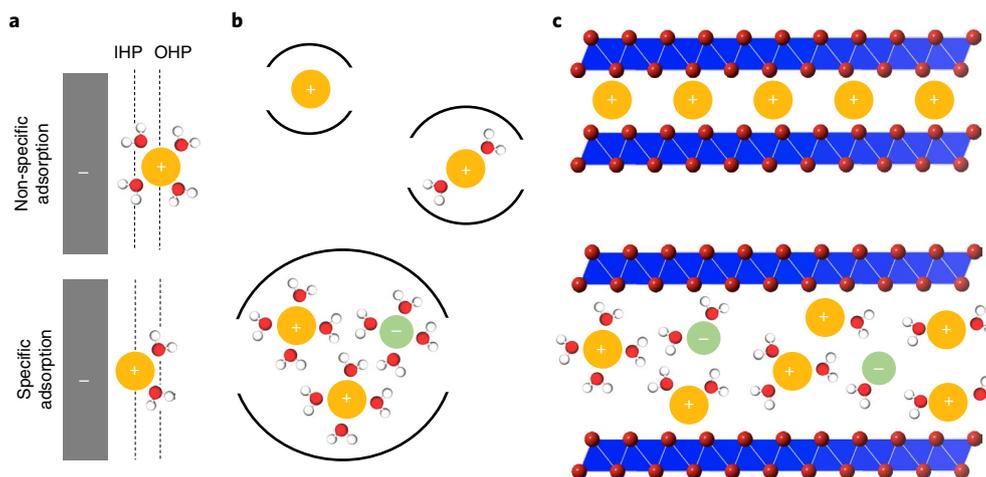
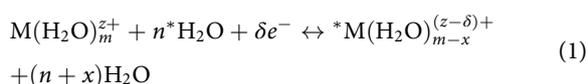


Fig. 1 | Overview of electrochemical interfaces with varying degrees of electrolyte confinement. **a**, Electrosorption at an ideal (planar) electrochemical interface, in which the degree of ion solvation defines whether the ion is non-specifically adsorbed (charge is induced, but not transferred) or specifically adsorbed (and undergoes charge transfer). **b**, Ion electrosorption under confinement within a typical porous carbon, in which the pore size determines the degree of ion solvation. **c**, Ion electrosorption under confinement within a layered material (between 2D layers), in which the interlayer distance determines the degree of ion solvation. O and H atoms are represented by red and white spheres, respectively. IHP, inner Helmholtz plane; OHP, outer Helmholtz plane.

with the electrode and is critically important to understand electrochemical capacitance under confinement. In the case of strong ion solvation, the electrode's interaction will be primarily electrostatic, in which ions remain in the outer Helmholtz plane. This type of interaction can be considered as the induction of charge at the electrochemical interface¹⁰. Ions that are not solvated or shed their solvation shell (at least partially) can undergo specific or quasi-specific adsorption in the inner Helmholtz plane and chemical bonding to the electrode¹⁰, the case that was termed adsorption pseudocapacitance by Conway³. The shedding of a solvation shell can be described as a charge transfer reaction between the electrode and adsorbed ion, as exemplified here for the case of the specific adsorption of a hydrated cation¹¹:



Here, $M(\text{H}_2\text{O})_m^{z+}$ represents a hydrated cation, $n^*\text{H}_2\text{O}$ represents electrode-surface-adsorbed water and $*M(\text{H}_2\text{O})_{m-x}^{(z-\delta)+}$ represents an electrode-surface-adsorbed cation. If the adsorbed electrolyte species are protons, then $\delta = 1$ (that is, the adsorption of protons is associated with a complete electron transfer). The charge-transfer reaction depends on the bonding between the ion and electrode, which depends on the state of ion solvation¹². It can thus be expected that ion solvation is also of critical importance for the type of ion-electrode interaction in nanoconfinement.

Confinement effects in double-layer capacitor materials

There has been great interest in understanding the relationship between the specific capacitance, the surface area and porosity of nanoporous carbon materials^{13–16}. Carbon-based EDL capacitors (EDLCs) show deviations from the planar electrochemical interface behaviour when EDL formation occurs in a nanoconfined environment (Fig. 1b). In a porous carbon electrode, the pore size is often smaller than the Debye length of the electrolyte¹⁷. The pore size can also be smaller than the solvated ion size, but larger than the bare ion size. For potentials less than the potential of zero charge, a decreased capacitance is observed due to ion sieving, which limits the transport of ions with effective sizes smaller than that of

carbon nanopores (Fig. 2a)^{13,14}. Confinement of ions in subnanometre pores can lead to their (partial) desolvation, which results in a capacitance increase, deviating from the linear dependence on the surface area¹⁵. Of particular interest is the appearance of reversible peaks on the capacitive double-layer cyclic voltammogram (CV) signature when the carbon pore size is close to the effective ion size (Fig. 2b). This additional reversible charge is hypothesized to originate from increased interactions between the ions and the carbon host in the confined nanopore environment when the ion solvation shell becomes (partially) stripped off^{8,19}.

Important understanding of the EDL under confinement comes from computational and theoretical studies directed towards understanding the role of the molecular and nanoconfined microenvironment in the performance of capacitive storage devices. As discussed in a recent review, these involve techniques from first principles through atomistic simulation to coarse-grained descriptions (such as classical density functional theory)²⁰. Many of these theoretical efforts were made to understand the increase of capacitance when the electrode pore size is comparable with the dimensionality of ionic species^{21–23}.

Even for solvent-free electrolytes, such as ionic liquids, confinement effects can cause an increased capacitance when the ion size matches the pore size²⁴. For example, Kondrat et al. pointed out that the surge in capacitance is caused by image forces that exponentially screen out the repulsion of the same-charge counterions inside narrow pores²⁵. The existence of a superionic state (creation of co-ion pairs), such as that theoretically predicted by Kornyshev's group, was confirmed experimentally by X-ray scattering of ionic liquid in 0.7 nm pores of carbide-derived carbon^{25,26}. Even though there is no solvent present in a classical sense, the disruption of the network (bulk order) of an ionic liquid (where anions typically surround cations) due to nanoconfinement was shown to increase the capacitance due to the increased presence of co-ions in the 'first solvation shell' of electrosorbed ionic liquid ions. Ions of the same charge can be present next to each other in narrow pores, thus 'breaking' the Coulomb law²⁶. These insights allow the effective tailoring of the carbon pore structure and the increase of the specific capacitance of nanoporous carbons²⁷. The effects of confinement on ion desolvation and/or arrangement in porous electrodes lead to deviations from the classic EDL model at the planar interface. This causes the

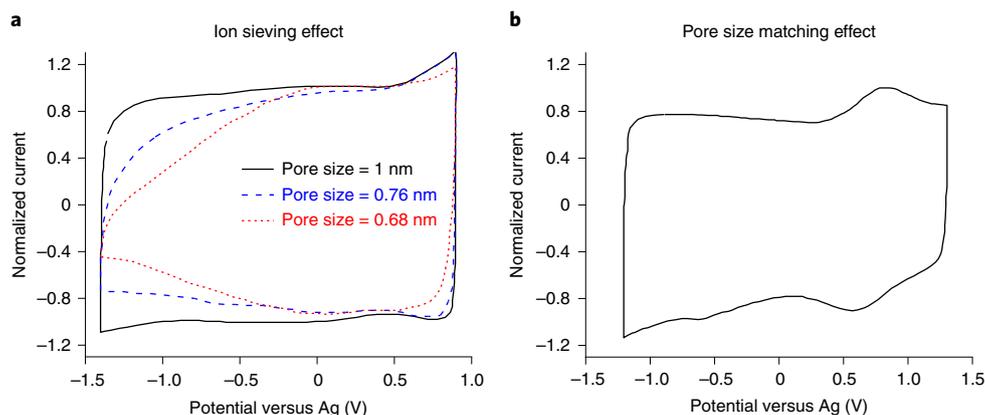


Fig. 2 | Examples of potential-dependent effects in carbon EDLCs. Nanoconfinement in pores (shown schematically in Fig. 1b) leads to deviation from flat electrochemical interfaces. **a**, Ion sieving during negative polarization of nanoporous carbons with pore sizes below 1 nm in 1.5 M NET_4BF_4 (tetraethylammonium tetrafluoroborate) in acetonitrile electrolyte. **b**, CV in 2 M EMI-TFSI (1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl) imide) in acetonitrile shows that when the effective ion size is close to the carbon pore size (1 nm here), a set of reversible peaks appears on top of the EDL capacitive signature. Figure adapted with permission from: **a**, ref. ¹⁴, Elsevier; **b**, ref. ¹⁸, Elsevier.

electrochemical signature of ion electro sorption processes to exhibit potential-dependent features (Fig. 2).

When using carbon, it is also important to consider the specific electronic structure of the respective carbon allotropes. As carbon is not an ideal metallic conductor, there is a unique potential-dependent space-charge capacitance. For graphitic carbons, the availability of charge carriers increases during polarization, which in turn increases the conductivity²⁸. As the insufficient supply of charge carriers within the solid limits the charge-screening ability at the fluid–solid interface, this leads to an additional space-charge-related increase in the capacitance of many carbon materials at increased potential²⁹.

Confinement effects in intercalation-type materials

Electrochemical ion intercalation into layered materials is commonly considered to involve complete charge transfer and measurable change(s) in the bonding of the electrode material. It can show electrochemical responses comparable with those of non-Faradaic EDL formation in nanoporous carbons, especially when interlayer molecules, such as water, organic solvents or functional groups, are present in the host material and there are no first-order phase transitions⁹. The origin of this effect is still a subject of debate. In general, we can differentiate between aqueous and non-aqueous electrolyte systems, but the phenomenon can be observed in both cases. Given the presence of highly mobile protons and many naturally occurring hydrated oxides (as opposed to materials with organic molecules confined in their interlayer space), the effect is more frequently observed in aqueous systems. The electrochemical intercalation of ions can then be regarded as lying on a continuum from the electro sorption phenomena described in the previous section.

A prominent example is the charge-storage behaviour of a hydrated layered transition metal oxide, birnessite, in neutral pH aqueous electrolytes³⁰. Some studies ascribe the observed capacitance to EDL formation⁶, whereas other works found changes in the crystal structure and Mn oxidation state during cycling, which points to a Faradaic, pseudocapacitive nature of charge storage^{31,32}. We have recently shown how these varying viewpoints of the capacitive behaviour of birnessite can be unified when the cation intercalation mechanism responsible for the capacitive response of birnessite is considered (Fig. 3)³³. Using a multimodal characterization and simulation approach, we found that the ion intercalation appears capacitive (lacks potential dependence) because K^+ intercalates into a hydrated interlayer. Simulations show that K^+ intercalates directly

in the middle of the interlayer, surrounded by H_2O molecules, and with relatively little structural change of the host.

These effects are also observed in systems using organic electrolytes. In MXenes³⁴, a growing materials family of 2D transition metal carbides, nitrides and carbonitrides, several recent studies analysed the effect of organic solvent co-intercalation and observed large effects on the electrochemical intercalation of lithium and sodium ions^{35,36}. MXenes possess a high electronic conductivity, but also transition-metal-oxide-like surfaces capable of reversible redox reactions. Wang et al. demonstrated that the co-intercalation of organic solvent with Li^+ in $\text{Ti}_3\text{C}_2\text{T}_x$ MXene reduces the total amount of stored charge³⁷, which strongly supports the hypothesis of a reduction in the ion–host interaction. First-principles calculations also found a dependence of the charge storage mechanism in MXenes on ion solvation, with partial desolvation leading to charge transfer between intercalated ions and surface termination, such as oxygen³⁸.

These studies provide clear examples of how capacitive behaviour lies on a continuum: double-layer formation in carbon nanopores that has been traditionally regarded as outer surface electro sorption shares similarities with ‘inner surface’ intercalation, as in birnessite MnO_2 or MXenes. In both cases, nanoconfinement within pores or the interlayer space, respectively, determines the charge storage characteristics.

Unified model of electrochemical charge storage under confinement

In the previous sections, we demonstrated that nanoconfinement may cause deviation in the adsorption behaviour of ions from the classical EDL model. This is true for materials typically employed in both EDLCs and intercalation-type batteries. The examples provided illustrate how confinement can lead to potential-dependent current features reminiscent of battery materials in EDLC materials, such as nanoporous carbons (for example, ion sieving or partial charge transfer for ion/pore size matching), as well as potential-independent current features in typical battery materials, such as transition metal oxides (for example, the intercalation of K^+ in birnessite in aqueous electrolytes) reminiscent of double-layer capacitors.

We illustrate this concept by considering the charge storage characteristics of lithium ions in the graphene system. The electrochemical response of graphene sheets in an organic lithium-containing electrolyte was studied by Hui et al. as a function of the number of graphene layers³⁹. The CV of single-layer graphene showed a

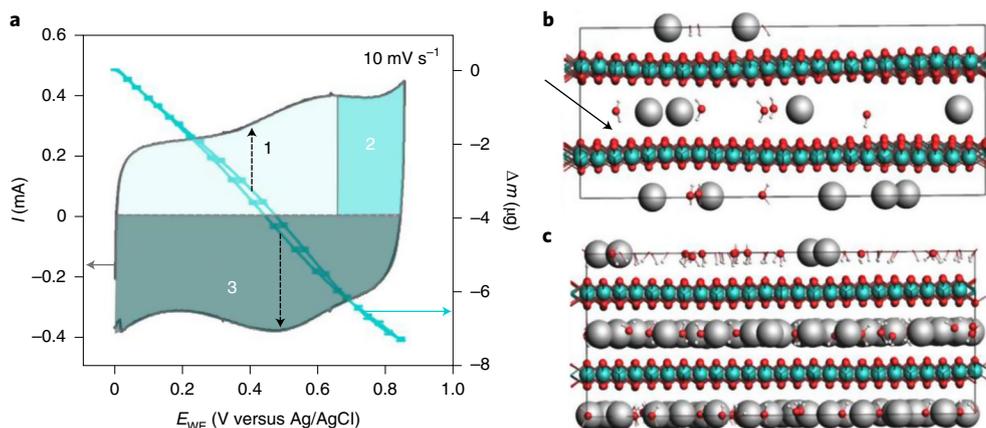


Fig. 3 | Cation intercalation into the hydrated interlayer of birnessite. **a**, The CV appears mostly capacitive, that is, it shows a potential-independent current. It correlates with a continuous, reversible change in electrode mass (Δm) measured with an electrochemical quartz crystal microbalance. Regions 1–3 represent different mass-to-charge ratios. WE, working electrode. **b**, Snapshot of a ReaxFF Grand Canonical Monte Carlo simulation of K^+ and H_2O intercalation into birnessite. The arrow indicates layer wrinkling due to the inhomogeneity of cation distribution. **c**, Snapshot after the interlayer is fully filled, which flattens the wrinkling in the simulation domain. Figure reproduced with permission from ref. ³³, Springer Nature Limited.

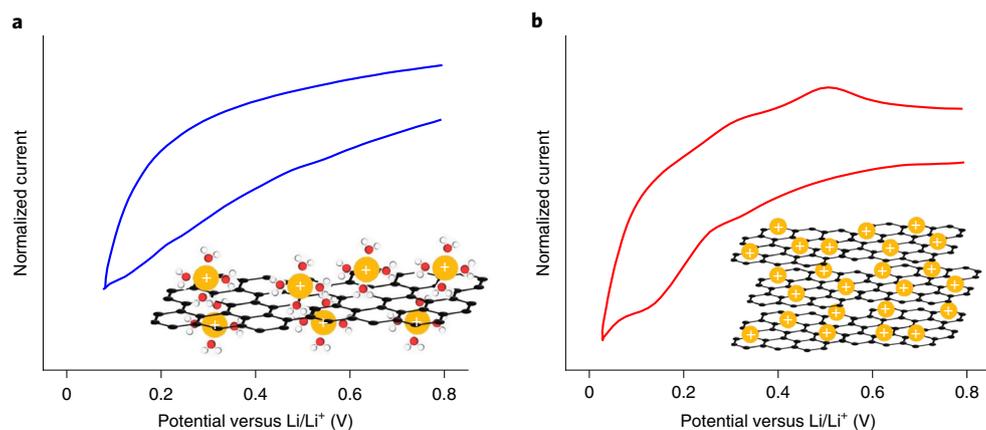


Fig. 4 | Influence of the number of graphene layers on Li^+ charge storage. **a, b**, Current-normalized CVs of single-layer graphene (**a**) and six-layer graphene (**b**) in a 0.1M $LiBF_4$ organic carbonate electrolyte. Insets: hypothesized Li^+ surface charge storage mechanism for **a** and Li^+ intercalation for **b**, which illustrate the transition from surface storage to intercalation based on the number of graphene layers. Figure reproduced with permission from ref. ³⁹, American Chemical Society.

potential-independent (capacitive) current response except at the cathodic potential limit (Fig. 4a). Such a response could occur from the adsorption of solvated or partially solvated Li^+ at the outer surface of the single-layer graphene, which is similar to the ideal interface shown in Fig. 1a. The current response is mostly potential independent because of the lack of specific adsorption and structural transitions in the graphene. Without other graphene layers, Li^+ adsorption can occur without a concomitant structural transition induced by the presence of other graphene layers, that is, in the absence of confinement. With an increasing number of graphene sheets, starting at four layers, redox peaks associated with the intercalation of desolvated Li^+ and staging mechanisms emerge in the CVs (Fig. 4b).

From this experimental data, we derive a thought experiment as to how the electrochemical signature of the system evolves if several single-layer graphene sheets are brought closer and closer together, up to the point of the interlayer distance of graphite (~ 0.33 nm). With the increasing confinement of Li^+ between the graphene layers, fewer solvent molecules are present within the interlayer space and, with that, the interaction between the host and Li^+ ions increases.

The higher density of the graphite due to the small interlayer spacing would also mean more interactions between the graphene sheets, which leads to the structural transitions that give rise to the staging mechanism. We hypothesize that this transition between solvated Li^+ adsorption on a single graphene sheet and the regular intercalation of desolvated Li^+ into graphite would occur with a continuous change in the charge storage behaviour, accompanied by changes in ion solvation, ion mobility and electrochemomechanical behaviour.

We propose a unified approach that involves a transition from the ‘binary’ view of electrochemical charge storage in nanoconfined spaces as either a purely electrostatic phenomenon or a purely Faradaic phenomenon. It should rather be regarded as a continuous transition between the two determined by the extent of ion solvation and ion–host interaction. This is the region in which some of the ‘pseudocapacitive’ processes are observed. It is similar to our understanding of chemical bonding, which is rarely ‘ideally’ a primary bonding type, such as covalent or ionic, or electrodes, which are rarely ideally non-polarizable (Faradaic) or polarizable (non-Faradaic). The same intermediate region exists between physisorption and chemisorption⁴⁰. Figure 5 illustrates how an increasing

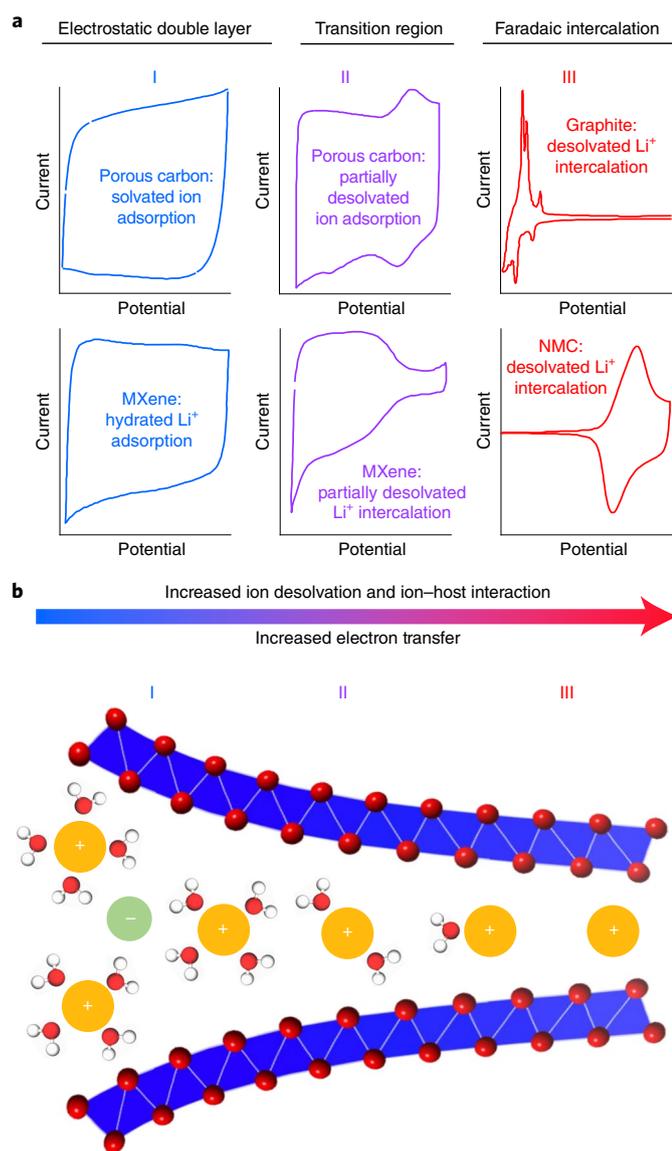


Fig. 5 | Unified approach to charge storage in nanoconfined environments.
a. Representative CVs demonstrate a continuous transition from electrostatic double-layer (I), through a transition region (II) to Faradaic intercalation (III) in nanoconfinement that is driven by the extent of ion solvation and the resulting ion-host material interaction.
b. Pseudocapacitive processes can lie in the transition region. The CVs in **a** represent typical behaviours and do not cover all possible cases. Panel **a** adapted with permission from: ref. ¹⁸, Elsevier (porous carbons); ref. ⁵⁸, The Korean Electrochemical Society (graphite); ref. ⁵⁹, Wiley (MXene hydrated); ref. ⁶⁰, Springer Nature Limited (MXene desolvated); ref. ⁶¹, IOP Publishing (layered $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$, NMC).

degree of confinement is accompanied by a decreasing degree of ion solvation, which leads to an increased ion–host interaction. This will cause a continuous transition from EDL formation, through a transitioning state to Faradaic intercalation for typical EDLC materials (top row of graphs in Fig. 5) and typical intercalation-type battery materials (bottom row).

Future opportunities and remaining challenges

Given the importance of electrochemical capacitance under confinement for many applications, future opportunities in this area must focus on atomistic understanding of the phenomenon to the

furthest extent possible. Therefore, studies of the electrochemical interface of porous and layered materials should aim for a detailed understanding of the mechanism by which charges are stored. To achieve this understanding, close collaboration between theory and experiment is required. From the modelling side, ab initio molecular dynamics augmented with machine-learning force fields are promising to gain an understanding of the coupling between electronic structure and ion distribution in confinement. Experimentally, the use of operando techniques to track structural or chemical changes of the electrode materials during electrochemical operation at timescales relevant to the charge storage process is particularly valuable, such as operando X-ray diffraction or X-ray absorption^{41,42}. Techniques capable of probing the composition, structure and dynamics of the confined electrolytes are also critical, such as in situ NMR⁴³.

Fundamental understanding of the EDL and ions in confinement will help to address many open questions of great practical importance for energy storage, conversion, water desalination and biology. Even a single electron transfer from the ion to the host in porous confinement may lead to the energy density of rechargeable batteries, but with the charging rates and lifetimes of EDLCs, as phase transformations and large strains can be eliminated. Can more than one electron per atom (or a larger charge, in general) be transferred in the case of multivalent ions? Capacitive storage with multivalent ions appears to be enabled by a nanoconfined environment⁴⁴ and could be a promising approach to increase the energy density of double-layer capacitors. The role of the density of states at the Fermi level in the electrode material on its charge storage ability has not been fully understood. Can electrode materials with metallic conductivity, but a tunable Fermi level, like MXenes or highly conductive transition metal nitrides⁴⁵, lead to a breakthrough in charge storage by providing more than one electron to multivalent cations? Can metallic MXenes minimize, or even eliminate, mirror charge and lead to a higher capacitance in porous confinement?

The ion population within a confined space is of equal importance in terms of the total number and type of ion transport kinetics. Ionophobic pores will exhibit the unique behaviour of being permselective on charging, as they only uptake counterions with no need to eject co-ions because the pore is initially empty. This is opposite to non-permselective charge storage processes in which co-ions and counterions are exchanged². Although for energy storage both processes yield the ability to store electric charge (and to do so efficiently), this is a key question for the field of water desalination: only permselective nanopores will enable electrochemical water desalination at a high molar strength⁴⁶. Electrochemical water desalination capitalizes on the concurrence of charge storage and ion storage for the purpose of water deionization. The time dependency in the ion populations in systems with multiple cations (and/or anions) is also of great importance for kinetic ion separation, in which selective ion adsorption in a subnanometre pore confinement is influenced by pore size, ionic charge and ion desolvation energies⁴⁷. For example, carbon micropores are known to be quickly populated by monovalent ions (like sodium), and yet, still during the charging process, all the sodium can be lost in favour of bivalent ions, like magnesium or calcium, so that no sodium ion is left in the pore during the discharge⁴⁸.

Narrow slit pores in graphene, MXenes and other 2D materials and their hybrids should allow the efficient sieving of ions for water deionization and various chemical separation processes. However, the issues of controlling the spacing between 2D nanosheets with the required accuracy and ensuring a sufficient electronic conductivity to enable the electrochemical control of transport in 2D confinement need to be resolved.

2D confinement between nanosheets allows swelling and contraction of the electrode on the intercalation and de-intercalation of ions, accompanied by counterions or solvent molecules, which

leads to a 'dynamic' EDL. Electrode swelling is undesired in energy storage devices and water deionization. However, a volume change with a small applied potential may be greatly important for energy-efficient actuation and soft robotics⁴⁹. Understanding of this process and coupling between electrochemistry and mechanics in such systems is needed. It can be achieved, for example, using electrochemical in situ and operando methods, such as atomic force microscopy⁵⁰ and dilatometry⁵¹.

Can the complete desolvation of ions and solvent rejection lead to increased electrolyte stability and an enlarged voltage window in energy storage systems by minimizing the degradation of solvent (or, in the case of ionic liquids, of the organic counterions)? Furthermore, can the confinement of molecules in those 2D slits reduce the activation barrier for an electrochemical reaction and allow a more efficient electrocatalysis? For ions electroadsorbed into micro- and nanoporous electrode materials, the change in the 'microenvironment' of the ion can be dramatic, depending on the pore chemical composition, geometry and average size and size distribution. Based on decades of experimental, theoretical and/or computational research in multiple fields on the impact of the nanoconfinement, we can expect that the pressure in the nanoconfined microenvironment may be orders of magnitude higher than that in the bulk⁵², chemical equilibria may be shifted by orders of magnitude⁵³, ion dynamics may be quantitatively⁵⁴ and even qualitatively changed (for example, Fickian diffusion replaced by single-line diffusion in sufficiently narrow cylindrical pores)⁵⁵, confined fluids may undergo order-disorder transitions⁵⁶ and adsorbed electrolyte concentrations may differ dramatically from that of the bulk electrolyte⁵⁷. Understanding confined electrochemical systems and the coupling between chemical, electrochemical and transport processes in confinement may open tremendous opportunities for energy applications in the future.

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Competing interests

The authors declare no competing interests.

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