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# **Advanced Characterization of Confined Electrochemical Interface in Electrochemical Capacitors**

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## **Abstract**

The advancement of high-performance fast-charging materials has significantly propelled progress in electrochemical capacitors (ECs). ECs store charges at the nanoscale electrode material/electrolyte interface, where the charge storage and transport mechanisms are mediated by factors such as nanoconfinement, local electrode structure, surface properties, and non-electrostatic ion-electrode interactions. This review offers a comprehensive exploration of probing the confined electrochemical interface using advanced characterization techniques. Unlike classical 2D planar interfaces, partial desolvation and image charges play crucial roles in effective charge storage under nanoconfinement in porous materials. This review also highlights the potential of zero charge (PZC) as a key design principle driving nanoscale ion fluxes and carbon-electrolyte interactions in materials such as 2D and 3D porous carbons. These considerations are crucial for developing efficient and rapid energy storage solutions for a wide range of applications.

## Introduction

Electrochemical capacitors (ECs), also known as supercapacitors, stand at the forefront of energy storage technologies<sup>1-2</sup>. Electrochemical Double Layer Capacitors (EDLCs), the main representative of EC family, operate through electrostatic ion adsorption into high surface area porous carbons, which forms an electric double layer (EDL) at the electrode/electrolyte interface<sup>3</sup>. Besides, pseudocapacitive materials store the charge by faradic pseudocapacitive process involving fast, surface redox reactions<sup>4-6</sup>. These mechanisms enable rapid charge transport, positioning ECs uniquely within the high-power, fast-charging segment of the energy storage market<sup>7-8</sup>. In recent decades, significant progress have been made in nanoscale engineering of EC materials, which include the development of high-performance electrodes<sup>9</sup>, innovative cell configurations<sup>7, 10</sup> like on-chip micro-supercapacitors and porous structures to emphasize electrolyte nanoconfinement effect at the nanometer and sub-nanometer scales to improve their charge storage capability<sup>11-14</sup>.

Capacitive energy storage, encompassing charge storage and transport at the nanoscale interface, presents significant complexity<sup>15-17</sup>, especially when subjected to nanoconfinement<sup>18-19</sup>. Different from classical 2D planar EDL, partial desolvation, partial charge transfer, and the generation of image charges onto host structures, have been identified also greatly enhance the energy storage capacity of confined EDLs<sup>12, 20-23</sup>. The confined ion-electrode interactions along with the effects of electrode material pore size, surface charge (e.g. surface termination and doping), and local disorder, significantly influence charge storage and transport<sup>24-28</sup>. However, the primary factors driving ion fluxes and boosting energy storage performance under nanoconfinement are still not fully understood. Recent advancements highlight the significance of characterization techniques in elucidating charge storage and transport mechanisms at the nanoscale<sup>3, 29</sup>. Visualizing ion fluxes is essential, which can be achieved by monitoring the variations in ion concentration, ion arrangement (location), electron density, ionic conductivity, conductivity of electrode materials, electrode

volume and mass during the electrochemical charging/discharging process. Extensive research has significantly advanced our understanding of ionic charge storage and transport processes. These studies have utilized a range of techniques and methods, including X-ray-based techniques<sup>30-34</sup>, atomic force microscopy (AFM)<sup>35-36</sup>, nuclear magnetic resonance (NMR)<sup>37-41</sup>, Raman spectroscopy<sup>42</sup>, X-ray photoelectron spectroscopy (XPS)<sup>43-44</sup>, electrochemical quartz crystal microbalance (EQCM)<sup>45-51</sup>, impedance-based<sup>12-13, 52</sup> methods, gating<sup>13</sup> methods, and artificial nanofluidic channels<sup>53-54</sup>.

Unlike many reviews that primarily focus on nanostructured materials used in ECs, this review aims identifying the factors that modulate nanoscale ionic charge storage and transport. It explores how advanced characterization techniques and methods can visualize ion fluxes under confinement in real-time, especially under dynamic conditions. These investigations pave the way for overcoming current performance limitations and achieving the next generation of efficient, high-performance materials and electrodes for ECs.

## Ionic Charge Storage at Nanoscale EDL Interface

**EDL at planar 2D electrode.** The Gouy-Chapman-Stern (GCS) model (**Figure 1a**) of the electric double layer (EDL) combines the Gouy-Chapman model<sup>55-56</sup>, which describes the diffuse layer of ions in a solution near a charged surface, with the Stern model<sup>57</sup>, which adds a compact counter-ion layer adjacent to the electrode surface. This model provides a more accurate representation of the EDL by accounting for both the diffuse and compact layers of charge.

The local structure of EDL is defined by the interfacial electric potential difference when an electrode is in contact with electrolyte. The structural and physical description of this interfacial region (considered as ideally polarisable interface) involves the distribution of free charges (ions), dipolar layers (solvents), and specific adsorption layers. There is a composition of the solution at which the electrode charge density ( $\sigma$ ) vanishes. Under this circumstance, the interfacial electric potential drop consists only of contributions from dipoles and specific adsorption layers. The corresponding electrode potential is termed as the potential of zero charge (PZC), a crucial characteristic of the electrode/electrolyte interface. A detailed physical origin of PZC can be found elsewhere<sup>58-59</sup>. It is worth noting that the PZC should not be confused with the Open Circuit Potential (OCP) where the net current is zero although in some situations, they may turn out to be the same. As the chemical potential is the driving force, the PZC is bounded to the surface energy (surface tension) as it is maximum at the PZC, as shown in the electrocapillary curve described by the Lippmann equation (**Figure 1b**), and corresponds to the minimum of the double layer capacitance<sup>60</sup>.

$$C_{dl} = \frac{\partial \sigma}{\partial \varphi} = -\left(\frac{\partial^2 \gamma}{\partial^2 \varphi}\right) \quad \text{Equation 1}$$

The PZC is a key parameter and can be viewed as a boundary between two main ion charge carrier regions. In fact, charge storage in the double layer can be achieved by counter ion adsorption (region I and II), co-ion desorption (region III and IV, **co-ion means ions with the same charge**) or in exchange (counter ion adsorption mixed with co-ion desorption, region V)<sup>29</sup> such as shown **Figure 1c**. The PZC that can be seen as a mirror image of the zeta potential<sup>24</sup> is then a key parameter to know, since it defines the transition between a negatively ( $\varphi < \text{PZC}$ ) and a positively charged ( $\varphi > \text{PZC}$ ) electrode surface in contact with an electrolyte. Experimental determination of PZC has been achieved by measuring the potential where the double layer capacitance is minimum<sup>61-63</sup> using electrochemical techniques or surface tension (contact angle) measurements. However, due to the porosity, pore connectivity, and polydispersity of porous networks, methods for quantifying the PZC of porous electrodes have not yet been established<sup>64-65</sup>. Developing advanced techniques to efficiently and accurately explore both the local and global PZC of porous electrodes is highly encouraged.

Recently developed in-situ technologies have also demonstrated remarkable capabilities in quantifying PZC<sup>60, 66-67</sup>. For instance, an in-situ optical setup has been used to assess the PZC by monitoring second-harmonic generation (SHG) changes that linked to the loss of structural–inversion symmetry of the interface<sup>68</sup> (**Figure 1d**). Findings revealed a PZC of the Pt–water interface of  $0.23 \pm 0.08$  V vs. SHE, which was independent of the electrolyte pH (from 1 to 13). This explains the enhanced catalytic performance for H<sub>2</sub> evolution in high pH electrolytes by a stronger interfacial electric field within the EDL<sup>66</sup>. The PZC value is also particularly significant in energy storage systems such as ECs, where the charge storage is achieved in the double layer, so that it has to be measured with the highest accuracy. In this context, in addition to conventional measurements, a scanning electrochemical microscope (SECM), equipped with a microelectrode detector, has been proposed as a powerful tool for measuring local PZC<sup>69-70</sup>. PZC is obtained by the charging current: a positive

charging current flows when the potential is more positive than the PZC, whereas a negative charging current flows when the potential is more negative than the PZC<sup>67</sup> (**Figure 1e**). In addition to SECM, Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) analyzes double-layer formation at the electrode/electrolyte interface<sup>43</sup> (**Figure 1f**). Charging the EDL broadens the full-width at half-maximum (FWHM) of core-level peaks from elements in the electrolyte, correlating charge accumulation and EDL capacitance at various potentials. Well-defined PZC values are obtained at the minimum FWHM in different electrolytes.

The application of well-accepted GCS model to real systems requires lower electrolyte concentrations (<0.1 M) and small polarisations. In contrast, EDL structure in highly concentrated room-temperature ionic liquid (RTIL) electrolytes, deviate significantly from classical GCS theory<sup>71</sup>. These deviations are often attributed to strong ionic Coulombic interactions and the charge overscreening<sup>72</sup>. **Figure 1g** illustrates that the electrode charge is overscreened by an excess of adsorbed counter-ions, which is then balanced by an additional layer of co-ions of the opposite charge. In addition to the overscreening effect, spontaneous ion/electrode surface interactions can modify the EDL structure at planar (conducting) electrode surface. When a single-layer graphene electrode (SLG) is immersed in neat 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (EMI<sup>+</sup>, TFSI<sup>-</sup>) ionic liquid electrolyte, EMI<sup>+</sup> cation chemisorb spontaneously onto the graphene surface due to strong  $\pi$ - $\pi$  interactions, even without polarisation. This process shifts the PZC to a significantly lower potential value (approximately  $-300$  mV)<sup>73</sup>. The resulting EDL primarily comprises EMI<sup>+</sup> cations, resulting in a charge storage mechanism driven by the change of cation orientation on the SLG surface<sup>63</sup>, facilitated by localized alteration of the electrolyte dielectric constant (**Figure 1h**). This example underscores the strong correlation between the non-electrostatic ion-electrode interaction ( $\pi$ - $\pi$  interaction in this case) and the PZC value, which is the key in determining the EDL structure and charge storage mechanism.



**EDL under confinement.** Moving from ideal, planar 2D electrode surface to realistic electrode materials for capacitive energy storage comes with the needs to take into account the effect of porosity and electrolyte confinement to depict the double layer structure. These effects involve various interactions among ions, solvents, and electrode host materials<sup>20, 74-75</sup>; confined geometries including nanopores<sup>11, 22, 76-77</sup> (e.g. porous carbon) and nanoslits in 2D layered materials<sup>21, 78-79</sup> (e.g. MXenes, reduced graphene oxides, and layered transition metal oxides). The utilization of 3D nanoporous carbon electrode materials with high specific surface area has been shown to significantly enhance the charge storage capacitance, and more specifically when electrolyte ions are confined in pores less than 1 nm<sup>80</sup>. Experiments and molecular dynamics simulation results suggested two origins for this capacitance increase: first, the charge overscreening observed at planar graphite electrodes is largely suppressed in nanopores<sup>11</sup> because of the limited space inside of nanopores, cutting off long range interactions; as a consequence, ions can access these nanopores following (partial) stripping of their solvation shell or reduction of their coordination number in ionic liquid electrolytes, which in turn shorten the charge screening length and allow ions to get closer to the carbon walls<sup>76-77</sup> (**Figure 2a**). A higher confinement degree means more carbon atoms in the ion surrounding, as a result, a shorter mean ion-carbon distance is reached: the capacitance increases accordingly (**Figure 2b**).

Thanks to their key features, including elemental specificity, high spatial and temporal resolution, time-resolved in-situ X-ray techniques have been used to investigate the double layer formation and structure in confined spaces during electrochemical processes<sup>35, 78, 81</sup>. A striking example lies in the combination of small-angle X-ray scattering (SAXS) technology together with Monte Carlo simulations that unraveled the mechanism of ion desolvation in three-dimensional microporous carbons<sup>32, 42, 82</sup>. More specifically, unconventional Coulombic ordering breakdown was revealed for highly confined ions within the nanopores (**Figure 2c**), resulting in the formation of co-ion pairs in pores since the space-limited nanopores can only accommodate a single

layer of ions. The experimental observation of the formation of co-ion pairs verified the existence of the ‘superionic state’ that was theoretically proposed by Kondrat and Kornyshev<sup>83</sup>, which implies a strong interaction between ions and the electrode surface<sup>31</sup>. The concept of the ‘superionic state’ theory was initially proposed to elucidate the observed increase in capacitance in microporous carbons in narrow slits or under confinement. The superionic state reduces interionic Coulombic repulsion through the generation of image charges, also known as mirror charges<sup>11, 24</sup>. When ions closely approach the conductive wall, as illustrated in **Figure 2d**, the confined cation induces mirror images with a negative sign, situated on the conducting wall<sup>87</sup>. The enhanced interaction (image charge interaction) between these image charges and host ions effectively overcame the electrostatic repulsion between closely packed co-ions<sup>84</sup>, particularly in narrow slits or under confinement. Materials possessing high electrical conductivity and an optimized pore structure are indeed highly desired to reach the ‘superionic state’, which in turn facilitates highly compact and efficient charge compensation<sup>85</sup>.

The local electrolyte organization in the confined space of electrode materials (such as nanopores or nanoslits) has been much investigated by in-situ nuclear magnetic resonance (NMR), as it can probe at local scale ion-electrode surface interactions<sup>37-38, 47, 86-88</sup>. When adsorbed ions come into close contact with  $sp^2$ -hybridized carbon walls, significant changes in the chemical shift ( $\delta$ ) of these ions are observed due to the presence of delocalized  $\pi$  electrons and ring-current effects in a magnetic field<sup>37, 39</sup>. The chemical shift difference ( $\Delta\delta$ ) between in-pore ions and neat electrolyte ions is correlated to the ion-electrode interaction (**Figure 2e**)<sup>89</sup>. Importantly, the change of in-pore ion populations under polarisation can be obtained from the in-pore resonance intensities of NMR spectroscopy. Consequently, different charge compensation mechanisms (e.g. counter-ion adsorption or ion exchange) can be monitored through in-situ NMR spectroscopy (**Figure 2f**)<sup>47</sup>.

A recent study, utilizing in-situ NMR spectroscopy, revealed an ion-specific nanoconfinement effect within multilayered graphene membranes (MGMs) featuring subnanometer-sized pores (ranging from 0.5 to 1.6 nm)<sup>39</sup>. While the electroneutrality breakdown occurring and spontaneous anion packing within confined nanopores has been validated by both experiments and modeling works<sup>31, 90-91</sup>. Notably, the solvent (water)-mediated ion-carbon electrode interaction has been identified as a driving force for co-ion packing under confinement, as evidenced by the in-pore ion concentration following the empirical Hofmeister series. Confined water plays a key role in this context: modeling work<sup>92</sup> has even proposed the concept of negative dielectric constant for confined water, also contributing to capacitance increase in nanopores/nanoslits. Additionally, experimental validation<sup>93-94</sup> has confirmed that the presence of structural water enhances charge storage capacity and facilitates rapid solid-state transportation.

In summary, the development of advanced characterization techniques has led to a better understanding of non-classical EDL formation and structure under confinement at nanoscale. From these macroscopic understanding, we found ion desolvation, creation of image charges into the carbon host structures, formation of co-ion pairs greatly contributed to enhanced charge storage. The microscopic origin of enhanced EDL-type (capacitive) energy storage performance lies in the neutrality breakdown and local dielectric constant increase, mediated by both the electrode (e.g. nanoconfinement) and the electrolyte (e.g. ion-specific effect). This highlights the key role of both desolvation and ion-electrode interactions in improving the localized charge density of the confined EDL by reducing the distance between the charge center and the electrode wall. These results pave the way for developing the next generation of ECs with fast-charging and high energy density key features, contributing to meet the growing energy demands the development of modern technologies needs<sup>95</sup>.

## Ionic Charge Transport Under Confinement

**Probing ion fluxes with electrochemical quartz crystal microbalance (EQCM) and combined techniques.** EQCM setup illustrated in **Figure 3a** has been the preferred technique for monitoring ion fluxes within electrodes during polarisation. EQCM uses piezoelectric effect of quartz crystals, enabling real-time monitoring of electrode mass change with high sensitivity up to nanogram level, according to Sauerbrey's equation<sup>48</sup>. Levi et al. has laid the foundation of using QCM sensor as a gravimetric probe, which allows tracking the mass changes that are correlated to ion fluxes into and out of the microporous activated carbons during electrochemical process<sup>96</sup>. The charging/discharging-induced repeatable electrode mass change (**Figure 3b**) was simultaneously measured by EQCM responses in 0.5 M aqueous CsCl electrolyte. This work revealed a strong dependence of the ionic fluxes on the electrode PZC. Indeed, the higher the overpotential with respect to the PZC, the more selective the electrode becomes, resulting in a balance of counter-ion charges, while around the PZC region the charge balance is maintained by both counter-ions (in) and co-ions (out). As aforementioned, since the PZC is a consequence of physical and chemical interactions between the electrode surface and the electrolyte, it has a key role on the charge storage mechanisms.

Experimental evidence of the partial desolvation of ions when entering nanopores have been obtained by EQCM measurements in various electrolytes<sup>24, 45, 97</sup>. Going beyond the pore size and pore size distribution, which drives partial desolvation, the electrolyte ion-electrode host interactions and local carbon structure have also been identified to play an important role in ion desolvation and the associated capacitance increase<sup>20, 25, 42, 73, 98-99</sup>. An obvious dehydration process of alkaline cations (e.g.  $Mg^{2+}$  and  $Zn^{2+}$ ) has been observed using EQCM (**Figure 3c**)<sup>25</sup>. Fully solvated cation adsorption was observed in multilayered reduced graphene oxide (rGO) surface under lower potential bias in chloride-based aqueous electrolytes, dehydration was

evidenced at higher cathodic potentials, where cation is in close contact with the electrode surface (Figure 3c). This cation dehydration was associated with enhanced charge storage capacity. Additionally,  $\text{Zn}^{2+}$  demonstrated a greater extent of desolvation and higher charge storage capacity compared to  $\text{Li}^+$  and  $\text{Mg}^{2+}$  in the same chloride-based electrolyte. Interestingly, the extent of cation desolvation was nicely correlated with increased cation-rGO interactions, as the zeta potential  $\xi$  (mV) of the carbon surface follows the trend:  $\xi_{\text{rGO-Zn}^{2+}} > \xi_{\text{rGO-Mg}^{2+}} > \xi_{\text{rGO-Li}^+} > \xi_{\text{rGO}}$ . Both the nature of the ion (ion size, charge density, hydration energy) and “non-electrostatic” ion-host interactions associated with the local ordering of the carbon (transition metal- $\pi$  interaction) drives the dehydration and capacitance under confinement<sup>25</sup>.

In essence, any physico-chemical interaction between the carbon surface and the electrolyte affects the overall charge storage mechanism. The PZC being the result of such specific interactions is due to the carbon’s local structure and/or functional groups. Last but not the least, the pore size (distribution) has been proven to play a major role, as it impacts the carbon-electrolyte interactions, consequently giving rise to more efficient charge compensation<sup>24</sup>. For instance, two CDC carbons were prepared at different temperatures: 800 °C (CDC-800) and 1100 °C (CDC-1100), both carbons have a similar porous volume and average pore size (0.9 nm), but the CDC-1100 prepared at the higher temperature has a more graphitized local carbon structure<sup>28</sup>. Both of the carbons delivered rectangular CV shape and ideal EDLC behavior in 2 M EMI-TFSI/ACN electrolyte (**Figure 3d** and **3e**). However, the ion flux tracked by the EQCM resonance frequency change ( $\Delta f$ ) shows different behavior: CDC-800 sample exhibited an expected counter-ion adsorption/desorption mechanism (Figure 3d), while CDC-1100 sample with more graphitic local structure demonstrated an expanded ion-exchange process (Figure 3e). It was found out this extended ion-exchange process lied from reinforced anion-graphitic carbon interactions in non-aqueous electrolyte, which results in PZC shift to a higher value ( $\Delta\text{PZC}=+0.2\text{V}$ ). **Figure 3f** illustrates the different mass uptake ( $\Delta m$ ) behavior with

charge accumulation ( $\Delta Q$ ), revealing that the total charge of CDC-1100 is lower than that of CDC-800, as expected for extended ion exchange process; besides, the limited positive potential window of CDC-1100, which arises from the positive shift of its PZC may also mitigate the charge accumulation. This work proposed that local carbon structure affect the ion flux by modifying the ion-electrode interaction, which has been further confirmed by a recent work using NMR spectroscopy technique<sup>27</sup>.

Another work in aqueous electrolyte shows that different ion fluxes were obtained by introducing in nitrogen containing functionalities (N-doping) nanoporous carbons which in turn give rise to different PZC. In non-doped YP-50F, a standard porous carbon material in ECs used as model material, the ion fluxes are driven by anion movement, due the low negative value of the PZC ( $-0.5V$  vs.  $Hg/Hg_2SO_4$ ). Differently, after N-doping (N-YP-50F), cation adsorption/desorption was found to be responsible for the charge compensation of the same carbon<sup>24</sup>. This shift was attributed to the stronger interaction between specific adsorbed anions and the N-YP-50F carbon surface. Indeed, it was evidenced N-doping leads to a decrease in zeta potential; and an increase of the PZC ( $\Delta PZC=+0.52V$ ) as they are negatively correlated. Thanks to an EQCM study, it was stressed out the key role of the local carbon charge (characterized by the zeta potential and the PZC) on the charge storage mechanism in porous carbons. The PZC is further evidenced as a strong indicator of electrolyte/carbon interaction, depending on several factors including the local carbon structure (e.g. ordering and doping) that can provide strong interactions with electrolyte ions. Although PZC indicates which ions are predominantly involved in the charge compensation, their role is further reinforced in highly confined environments. In nanopores, ions undergo (partial) desolvation, enhancing their interaction with the carbon material. This increased interaction strength contributes to more effective charge compensation.

Interestingly, the importance of the ion-electrode material interactions on their capacitive behavior has also been highlighted beyond carbon materials like MXene<sup>97</sup>

and  $\text{MnO}_2$ <sup>20</sup>. MXene and  $\text{MnO}_2$  are the typical materials that store the charge through rapid surface redox reactions on the transition metal element, resulting in an electrochemical signature similar to that of porous carbons<sup>100</sup>. Shpigel and co-workers investigated the possibility for anions insertion into MXene via EQCM with dissipation monitoring<sup>97</sup>. Interestingly, only cation flux has been probed across the entire potential window: cation insertion counterbalances the negative charge ( $\phi < \phi_{\text{PZC}}$ ), while cation extraction screens the positive charge ( $\phi > \phi_{\text{PZC}}$ ). This work highlights the electrostatic repulsion between terminated MXene surfaces and intercalated anions, which hinders anions insertion. Surface terminations changes the electrolyte-electrode interaction, which consequently controls the ion flux<sup>25-26</sup>.

EQCM can also allow for correlating the current ( $-\text{d}\Delta Q/\text{d}t$ ) to the rate of mass change ( $-\text{d}\Delta m/\text{d}t$ ) through ‘gravimetric cyclic voltammograms’ (gCV). The gCV of the pseudocapacitive  $\text{MnO}_2$  birnessite electrode displays a pair of broad and reversible peaks that align with those of the cyclic voltammetry curve, strongly suggesting that these current peaks are intimately linked with the mass change, or in other words, ion (de)intercalation<sup>20</sup>. A similar concept, defined as ‘mechanical cyclic voltammograms’ (mCV), was designed by monitoring the local deformation of electrode materials ( $\text{d}\delta$ ) using atomic force microscopy (AFM) and differentiating the deformation with respect to time ( $-\text{d}\delta/\text{d}t$ )<sup>101</sup>. The mCV aligns with electrochemical CVs in the case when the ion insertion-induced deformation scales linearly with the accumulated charge. Considering this characteristic, mCV offers advantages such as being unaffected by global resistance and insensitive to side reactions that may arise during cycling. Moreover, EQCM allows for deconvoluting the real-time fluxes of electrolyte species (e.g.  $\text{H}_2\text{O}$  and  $\text{H}^+$ ) during the CV scan. The reconstructed  $\text{H}^+$  and  $\text{H}_2\text{O}$  flux-based cyclic voltammograms ( $\text{H}^+$  J-CV) presents the potential depending  $\text{H}^+$  and  $\text{H}_2\text{O}$  fluxes and indicates the real-time hydration evolution of  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene in 1M  $\text{H}_2\text{SO}_4$  electrolyte<sup>102</sup>.

The combination of EQCM with other operando techniques has also shown to be highly effective for bringing key information on the charge storage mechanisms in capacitive electrodes. Electrochemical dilatometer (ECD) is another operando techniques that combines electrochemical cell and displacement measurements system<sup>103</sup>. In fact, A recent work investigated the charge storage mechanism in reduced graphene oxide materials (rGO) by combining EQCM and ECD<sup>25</sup>. The equivalent molar weight  $M_w$  obtained from multi-linear fitting of  $\Delta m \sim \Delta Q$  plot via EQCM measurement demonstrates two regions for cation ( $Mg^{2+}$ ) adsorption on rGO electrode as shown in Figure 3c: hydrated cation adsorption in region I corresponding to low cathodic polarisation and ion dehydration region II with high cathodic overpotentials. While  $Mg^{2+}$  adsorption leads to a linear volume expansion across the two regions despite dehydration occurs in region II. The consistent volume change rate strongly indicates continuous electrostatic volume expansion at shallow adsorption sites across the two regions and partial dehydration locally occurs at less accessible surface and more negative potentials.

Raman spectroscopy is an exceptionally sensitive technique for exploring the electronic and crystallographic structures of carbon materials<sup>104-105</sup>. The combination of EQCM and in-situ Raman spectroscopy has been used to study structural transformations of carbon electrodes during electrochemical polarisation<sup>106</sup>. Traditional EDL formation typically leaves the Raman features of graphene-like materials unchanged. This includes the positions and band shapes of the D, G, and 2D bands, resulting from the relatively weak interaction between adsorbed ions and the electrode within the classical EDL structure<sup>42</sup>. Nevertheless, a recent study revealed that formation of layered confined EDL in graphene-based materials with 0.7 nm layered channels leads to the splitting of the G band in two distinct peaks<sup>106</sup>. Those peaks correspond to a charged contribution (with a higher charge density) associated with the  $G^+$  band and an uncharged contribution (with little or no charge accumulation) linked with the  $G^-$  band (**Figure 3g**). Interestingly, the charge density calculated from



Raman spectra falls within the range of 0.009 to 0.011 electron charges per carbon atom within the confined interface. This value is one to two orders of magnitude higher than what is typically observed in a conventional EDL interface. These induced charges estimated from in-situ Raman spectroscopy were further combined with the electrode mass change obtained via EQCM during the charging and discharging processes (**Figure 3h**). The change of mass uptake is well in line with the increased band area ratio of the  $G^+$  band to the  $G^-$  band ( $A_{G^+}/A_{G^-}$ ), indicating that the ratio of highly charged carbon atoms is highly correlated with the continuous insertion of partially hydrated  $K^+$  ions<sup>42</sup>. Highly localized charges (insert of **Figure 3h**) present in the charged segments suggest a robust and direct interaction between electrolyte ions and the carbon host under confinement, which further confirms that confined EDL formation results in increased charge storage capacitance.

Moreover, EQCM can also be applied to emerging metal-organic framework (MOF) materials for capacitive energy storage<sup>107</sup>. The ionic fluxes tracked by real-time monitoring the electrode mass change suggested an important neat solvent loss/gain when charging/discharging the confined MOF pores (with diameter approximately 1.5 nm). The local in-pore solvent depletion during charging process accordingly accounts for the sluggish charging kinetics. Detailed analysis of ion fluxes and desolvation maybe limited in some cases - when multiple species or light element such as protons are involved for instance - as EQCM only measure a global weight change. In those cases, decoupling the accurate contributions of each flux (cation, anion, and solvent) requires additional techniques to be used in a combined approach, such as in-situ NMR spectroscopy<sup>47</sup>. AC-EQCM has also been proposed to deconvolute the signals coming from anions, cations and solvent, but such analysis needs complex signal processing which may limit the use of this technique<sup>108</sup>. NMR spectroscopy exploits the magnetic properties of specific isotopes of elements. Only nuclei with a non-zero magnetic moment (e.g.,  $^1H$ ,  $^{13}C$ ,  $^{23}Na$ ,  $^{31}P$ , etc.) are NMR-active. The main challenges of using NMR spectroscopy are the signal overlap from different environments of the

same element and signal broadening in materials with high magnetic susceptibility. Interesting readers can refer to these references<sup>109-110</sup> to get detailed insights about the limitations of several techniques discussed in this review.

### **Probing ion transport capability with impedance-based techniques.**

Electrochemical Impedance Spectroscopy (EIS) is a widely used technique for assessing the resistance/conductance of electrodes immersed in electrolyte across a broad frequency range. Conventional EIS measurement is conducted under a constant bias potential once the steady state is reached, but *operando* measurement is not allowed. Different from traditional setups, AC in-plane electrochemical impedance spectroscopy facilitates in-situ and *operando* monitoring for understanding the kinetic properties at electrode/electrolyte interfaces (**Figure 4a**). In this design, the electrode film is coated onto an insulating substrate (polymer film for instance), and two distinct potentiostats are used: one (P1) for polarisation of the electrode and the other (P2) for the AC impedance measurement within the plane of the electrode. The technique allows for the deconvolution of ionic and electronic percolations within the electrode plane (porous carbon for example) upon polarisation<sup>52</sup>. Results show a decrease of both electronic and ionic resistance during charge injection vs. PZC, leading to carbon doping in both the positive and negative directions (**Figure 4b**). This reduction in resistance might be attributed to enhanced conductivity due to ion confinement within the porous carbon structure, potentially accompanied by volume expansion. This AC in-plane impedance spectroscopy technique thus emerges as a useful tool for the monitoring of in-plane electronic percolation in electrodes during electrochemical operations. While *operando* AC in-plane impedance spectroscopy measurements allow accessing the change of the electrode impedance during the polarisation, this impedance change may have several origins (doping of the material by charge injection, electrode volume change etc.), so that it is sometimes difficult to make correlations. Also, the quality of the measurements must be validated by plotting the so-called ‘contour plot’<sup>111</sup> to ensure that the system is analyzed within the right frequency range to get reliable results.

In addition to *operando* tracking the electronic and ionic percolations as discussed above, the interactions between electrons that reside in the graphene lattice and the ions adsorbed on the surface of individual graphene sheets also needs to be

investigated. The ionic charging state of graphene-based electrode materials can alter its electronic conductance. This change induces a collective electrolyte gating effect, which enables real-time electrical probing of the charging dynamics electrically<sup>12</sup> (**Figure 4c**). Multilayered graphene-based nanoporous membranes (MGMs) with controllable pore size were used as model materials. These distinctive nanoheterostructures, composed of both electrons and ions, exhibit a unique configuration wherein the electrons within graphene are confined within atomically thin sheets, while ions reside within nanoscale channels. The electronic conductance of MGMs can be measured under different gating voltages ( $V_g$ ) by charging MGMs at a constant current using the galvanostatic cycling with potential limitation (GCPL) technique. Experimental results have demonstrated a reversible alteration in the electronic conductivity of these electrodes under polarisation. Notably, no hysteresis was detected for electrodes with larger average pore sizes (5.0 nm and 2.0 nm). However, when subjected to extreme nanoconfinement with pore sizes of 0.8 nm and 0.6 nm, a non-linear response in the change of conductivity relative to gating voltage was observed (**Figure 4d**). This suggests a time-delayed polarisation effect, indicative of ‘memory effect’ with a slower ionic response. Such a delayed ionic response could stem from ion reorganization with steric effects. Another plausible explanation is the limited ion transport due to enhanced interactions between ions and pore walls. In this state, ions confined within exceptionally small pores may exhibit unique behaviors under dynamic conditions. Similar to AC in-plane impedance measurement, the data obtained from gating setups can be convoluted and the complexity of nanoconfined EDL makes it difficult to fully understand the precise mechanism. Besides, achieving proper alignment and contact between the gating electrode and the sample can hamper the experiment reproducibility. It is also worth mentioning the frequency range of the impedance has to be spot on since the cell time constant can interfere with obtaining accurate electronic conductance measurements.

**Probing ion fluxes with artificial nanofluidic configurations.** Figure 5a demonstrates surface force balance (SFB) technique<sup>112</sup>, utilizing force analysis models, has offered valuable insights into the charging dynamics of individual nanoslit across a range of pore widths. This method tracks transient surface force changes as ions are transported from the bulk electrolyte to the charged interface under fixed external potentials, with typical response timescale shorter than  $10^{-9}$  seconds. Charge accumulation bends a calibrated spring, leading to an observed change in separation ( $\Delta D$ ), as depicted in **Figure 5b**. This separation gradually returns to initial value as charge redistribution. Results show that a longer charging time is required to establish EDL along the pore as the thickness (pore size) of the nanoslits decreases. Similarly, atomic force microscopy (AFM) technique, based on force response as well, has also revealed a delayed ion transportation within carbon pores when the pore size decreasing from 8 nm into 1.2 nm<sup>113</sup>. These findings of sluggish ion transport within confined channels align well with previous studies as evidenced by impedance<sup>12</sup>, NMR<sup>41</sup> and cavity micro-electrode techniques<sup>114</sup>.

Different from SFB technique that tracks force change, transient single-particle imaging<sup>18</sup> technique tracks ion transport in nanochannels by monitoring changes in scattering light intensity (**Figure 5c**). When an external electric field is applied to gold nanoparticles (AuNPs), counter-ions move into the nanochannel, altering the local refractive index (RI) and causing a relaxation of optical signals. This process reaches a plateau when electronic charge is fully shielded (**Figure 5d**), offering microsecond-level temporal resolution for real-time observation of charge relaxation during EDL formation. Anomalous dynamics observed in short nanochannels contradict classical transmission line models, indicating a change in the diffusion coefficient likely due to steric hindrance near the electrode surface. This sluggish ion mobility near the electrode slows EDL formation, underscoring the complexity of ion transport in confined environments.

Contrary to most experimental findings on delayed ion transport in nanoconfined channels, an anomalous enhancement of electrolyte ion diffusion has been observed through layered graphene-based nanoporous membranes<sup>54</sup>. By controlling the nanoslit sizes of these membranes, the tunable nanoconfined environment achieved allows for reversible modulation of sub-2 nm ion diffusion through surface potential-induced EDL effects. Unlike in bulk electrolytes, the short-range and ion-specific ion-ion correlations under severe nanoconfinement are believed to explain this enhanced ion diffusion. Moreover, given the substantial experimental challenges in investigating nanoconfined ion transport, the development of modeling<sup>115</sup>, machine learning<sup>116</sup> and equivalent circuit models<sup>39</sup> has greatly contributed to this field. These findings emphasize the importance of ion-ion correlations, confinement (nanoslit sizes) in influencing ionic transport under strong confinement. This offers promising prospects for designing efficient charge transport mechanisms to achieve high-performance ECs.

Thanks to the aforementioned techniques and setup to study nanoscale ion transport mechanisms. A novel current regulator device was designed to achieve bias-direction-adjustable current rectification. Based on the sieving effect of carbon electrodes with high surface area and selected pore size, controllable ion flux was achieved by blocking electrolyte ions from entering sub-nanometer pores. This resulted in the development of capacitive analogues of semiconductor diodes (CAPodes) with a high rectification ratio of up to 96.29%. CAPodes, as a generalized concept, are expected to be integrated into logic gate circuit architectures to implement logic operations, presenting a new avenue for energy-efficient and nature-inspired next-generation computing devices<sup>117</sup>.

In summary, we have demonstrated how to probe confined ion fluxes using various electrochemical techniques and nanofluidic channels in this section. These methods enable the monitoring of changes in mass (EQCM), volume (ECD), electronic structure (Raman and impedance spectroscopy), force (SFB), and optical properties (scattering intensity). Notably, PZC emerges as a crucial factor influencing ion fluxes

at the nanoscale. This significance arises from the PZC being a consequence of electrode-electrolyte interactions, further influenced or modulated by increased confinement. The precise control of PZC has been identified as essential for improving the charging kinetics and capacity of electrochemical cells.

## **Conclusion and Perspectives**

The ongoing pursuit of fast-charging energy storage devices, such as electrochemical capacitors (ECs), which aims at increasing energy density and long-term cycling stability, relies crucially on a profound understanding of EC materials at the nanoscale. In this review, we have emphasized cutting-edge techniques and technologies that have been of great help to elucidate the charge storage mechanisms at the nanoscale in EC electrode materials. In contrast to the conventional 2D planar EDL model, 3D nanoconfined EDLs store charges more efficiently, thanks to key factors including partial desolvation, image charges, and electroneutrality breakdown. Importantly, alongside the electrode pore size effect, the local carbon structure (doping, ordering, termination), and non-electrostatic ion-electrode interactions (e.g.  $\pi$ - $\pi$  interaction and transition metal cation- $\pi$  interaction) collaborate to determine the charge storage capacity of EC materials. When discussing carbon local ordering, it is essential to recognize that curvature is required in order to increase specific surface area of carbons, which results in the presence of not only ordered 6-atom rings but also various pentagons and heptagons. Additionally,  $sp$ - (linear chains) and  $sp^3$ -bonded atoms are present in the final structure of porous carbons. As a result, distinguishing the impact of the local carbon structure from the porosity can be challenging. Moreover, we showcased the real-time probing of ion flux under confinement and highlighted the key importance of the potential of zero charge (PZC) as a significant design principle to define the nature of ion fluxes. Ion dynamics and ion transport mechanisms under confinement are highly dependent on factors such as pore size, pore shape, pore surface properties (e.g. surface charge), and spontaneous ion-electrode interactions, as a result of the carbon local ordering.

The potential of zero charge (PZC) plays a crucial role in defining ion flux and can be carefully engineered, for example, by altering or enhancing non-electrostatic ion-electrode interactions, which are further influenced by porosity (nanoconfinement), carbon surface groups or carbon local structure. For a single electrode design, a higher PZC value leads to a charge storage mechanism predominantly involving cation fluxes, while a lower PZC results in major anion contribution. Shifting the PZC to a desirable value allows for the selection of specific ionic charge carriers, which is key for energy storage systems. Avoiding PZC located in the middle of the electrochemical potential window (EPW) is expected to avoid ion exchange (crowding). Besides, positioning the PZC at one end of the EPW can maximize the interfacial voltage difference (vs. PZC) and store more charges for a specific charge carrier (either cation or anion). As a result, optimizing the PZC is also important for enhancing cell-level performance by maximizing the energy storage capacity of each electrode. Finally, the degree of carbon disorder is an important parameter to optimize the capacitance of porous carbons, such as recently shown by Liu et al., although it is difficult to completely decorrelate it from the PZC value, as the resulting capacitance is an interplay between the carbon surface and the electrolyte, involving anions, cations, and solvent molecules.



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### **Ethics Declarations**

The authors declare no competing financial interest.

### **Additional Information**

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## Figure Captions

**Figure 1. Electric double layer (EDL) formation at 2D planar interface.** (a) Classical EDL structure at 2D planar interface. (b) Relation between surface tension ( $\gamma$ ) and potential ( $\phi$ ) of charged interface, with potential of zero charge (PZC) located at the maximum of  $\gamma$ - $\phi$  curve. (c) PZC drives the ion flux. (d) Optical second-harmonic generation (SHG) spectroscopy for detecting the PZC. (e) Scanning electrochemical microscopy setup with a microelectrode to measure the PZC. (f) Ambient pressure X-ray photoelectron spectroscopy (APXPS) for detecting the EDL structure and the PZC. (g) charge overscreening on 2D planar electrode surface in solvent-free ionic liquid electrolyte. (h) EMI<sup>+</sup> cation reorientation for balancing the charges at negatively polarised single layer graphene interface. Panel (e) adapted with permission from ref. <sup>67</sup>, American Chemical Society.

**Figure 2. EDL under confinement.** (a)-(b) Molecular dynamics simulations of electrostatic adsorption of PF<sub>6</sub><sup>-</sup> anions in acetonitrile electrolyte at nanoporous carbon interface. Four different adsorption modes for the molecules have been defined: edge, plane, hollow and pocket site with increasing confinement degree. (a) The average solvation number of PF<sub>6</sub><sup>-</sup> anions decreases when bulk electrolyte ions approach hollow sites. Insets suggest more carbon atoms coordinated with the PF<sub>6</sub><sup>-</sup> anion and less solvent molecules at hollow site (the solvation state of bulk electrolyte ions is similar to edge sites with less confinement). (b) Changes in the ion distribution at four active sites under different potentials. PF<sub>6</sub><sup>-</sup> anions transport into more confined sites, e.g. hollow site under positive polarisation (+0.5V). Inset shows carbon atoms coordinated with confined PF<sub>6</sub><sup>-</sup> anion. (c) co-ion pair formation and partial breaking of Coulombic ordering of EMITFSI ionic liquids under micropore confinement with average pore size 0.7nm. (d) Schematic drawing of the image charges and image charge interactions under confinement. Electrolyte cations (red) placed between two conducting surfaces mirrors image charges (blue) on the other side of the conducting walls. The image charge interaction (dashed line with arrows) overcome the repulsive interaction between confined cations and reinforces the charge screening. (e) <sup>19</sup>F magic angle spinning (MAS) NMR spectrum of YP50F carbon film soaked with NEt<sub>4</sub>BF<sub>4</sub>/dACN (1.5 M) and the neat electrolyte. The ex-pore BF<sub>4</sub><sup>-</sup> anion resonance close to that of neat electrolyte while the in-pore BF<sub>4</sub><sup>-</sup> anion delivers resonance at shielded chemical shift.  $\Delta\delta$  is defined as the difference between the chemical shift of the in-pore resonance ( $\delta_{\text{in-pore}}$ ) and that of the neat electrolyte ( $\delta_{\text{neat-electrolyte}}$ ). (f) In-pore ion populations calculated from the resonance peak of NMR spectrum for supercapacitor electrodes under different cell potentials (-1.5V to +1.5V). Considering the Potential of Zero Charge (PZC, +0.49V vs. Ag) is close to Open Circuit Potential (OCP, +0.43V vs. Ag), different ion fluxes are present as: ion exchange for positive charging ( $\phi > \phi_{\text{PZC}}$ ) whereas cation adsorption dominates for negative charging ( $\phi < \phi_{\text{PZC}}$ ). Adapted with permission from ref. <sup>77</sup>, Springer Nature Ltd (a) and (b); ref. <sup>47</sup> Springer Nature Ltd (e).

**Figure 3. Probing ion fluxes with electrochemical quartz crystal microbalance (EQCM) and combined technologies.** (a) schematic illustration of EQCM setup: combination of quartz crystal microbalance (QCM) and three-electrode electrochemical cell. Active material-coated quartz crystal sensor serves as working electrode, the electrode mass change is real-time monitored by the change of resonance frequency from QCM. (b) Characterization of a microporous activated carbon in an aqueous solution of 0.5M CsCl by EQCM. The electrode polarisation (bottom curve) drives the mass change (top curve) with sketch showing the ion flux on the right panel. The pink and the orange shadowed area represent the cation flux and anion flux, respectively. The position of the PZC is shown by the blue dots and dotted blue line. (c) Two regions of alkaline metal cation adsorption on rGO surface: hydrated cation adsorption in region I under low polarisation (left) and cation dehydration in region II under higher polarisation (right). The integrated capacitance increases after cation dehydration (middle). (d)-(e) CV and EQCM frequency response ( $\Delta f$ ) of (d) non-graphitic CDC-800 and (e) graphitic CDC-1100 microporous carbon-coated Au electrodes in 2 M EMI-TFSI/ACN electrolyte at a scan rate of  $10 \text{ mV s}^{-1}$ . (f) Electrode mass change calculated from the EQCM response vs. charge during the polarisation of non-graphitic CDC-800 and graphitic CDC-1100 carbon electrodes. (g) G band splitting in the in-situ Raman spectra of the layer-confined graphene-based electrode during the EDL charging process (h) The variation of the electrode mass change (solid black line) and its Raman feature (orange line) during the layer-confined EDL charging process (partial hydrated  $\text{K}^+$  insertion). Adapted with permission from ref. <sup>96</sup>, Springer Nature Ltd (b); ref. <sup>25</sup>, Springer Nature Ltd (c); ref. <sup>42</sup>, Wiley (g) and (h).

**Figure 4. Probing ion transport capability with impedance-based technology.** (a) experimental electrochemical cell setup for in-plane impedance setup. The changes in the in-plane electrode resistance under potential can be assessed. Two distinct potentiostats were employed, the first potentiostat (P1) applied a constant potential to the electrode material to reach a steady-state condition. The second potentiostat (P2) was utilized to monitor the in-plane AC and DC impedance throughout the potentiostatic experiments. (b) Ionic and electronic resistance change of porous carbon electrode under different polarisation potentials in a static model, measured in ionic liquid EMITFSI electrolyte. (c)-(d) Probing nanoconfined ion flux by operando impedance spectroscopy with electrolyte gating technique. (c) schematic illustration of the supercapacitor-like electrochemical setup used to investigate the electrolyte gating effect in multilayered graphene-based nanoporous membranes (MGMs). The transmembrane conductance ( $G_{\text{MGM}}$ ) is measured upon applying gating potential ( $V_g$ ) between the counter (or gate) and working electrodes, both composed of MGMs. (d) electrode hysteretic conductance response vs. gating potentials during galvanostatic charging/discharging cycles with 0.6 nm interlayer distance. The charging rate is set at  $0.5 \text{ A g}^{-1}$ , and aqueous 1 M BMIMBF<sub>4</sub> is applied as electrolyte. Adapted with permission from ref. <sup>12</sup>, Springer Nature Ltd (c) and (d).

**Figure 5. Probing ion fluxes with nanofluidic channels.** (a) Schematic of surface force balance (SFB) with a three-electrode electrochemical cell to probe ion dynamics. Electrodes

are immersed in electrolyte within a quartz bath to prevent current leakage. Gold surface potentials are within the double-layer range to avoid electrochemical reactions. Gap distance ( $D$ ) between gold and mica surfaces reveals pore-like structure. (b) Magnified view of distance change ( $\Delta D$ ) during electrochemical charging and relaxation process.  $\Delta D$  exhibits asymmetric shape and shifts from initial surface separation when potential is applied, reaching extreme values and recovering to pristine value during relaxation. (c)-(d) Tracking ion transport kinetics under nanoconfinement. (c) Setup for monitoring ion charging kinetics on gold surface. Gold particles (AuNPs) serve as working electrode, with counter and reference electrodes forming a three-electrode in-situ electrochemical cell. Electrolyte ions migrate inside silica nanochannels on AuNPs surface under applied potentials, altering scattered light intensity. (d) Optical signals evolution with time after electrochemical operation. Charging time constant ( $\tau_{EDL}$ ) can be obtained by fitting scattering light signal. Adapted with permission from ref. <sup>112</sup>, Wiley (c) and (d).