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Computational Insights into Charge Storage Mechanisms of Supercapacitors

Kui Xu, Hui Shao, Zifeng Lin* , Céline Merlet, Guang Feng , Jixin Zhu*, and Patrice Simon

Computational modeling methods, including molecular dynamics (MD) and Monte Carlo (MC) simulations, and density functional theory (DFT), are receiving booming interests for exploring charge storage mechanisms of electrochemical energy storage devices. These methods can effectively be used to obtain molecular scale local information or provide clear explanations for novel experimental findings that cannot be directly interpreted through experimental investigations. This short review is dedicated to emphasizing recent advances in computational simulation methods for exploring the charge storage mechanisms in typical nanoscale materials, such as nanoporous carbon materials, 2D MXene materials, and metal-organic framework electrodes. Beyond a better understanding of charge storage mechanisms and experimental observations, fast and accurate enough models would be helpful to provide theoretical guidance and experimental basis for the design of new high-performance electrochemical energy storage devices.

1. Introduction

Electrochemical energy storage devices, including supercapacitors and batteries, can power electronic/electric devices without producing

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greenhouse gases by storing electricity from clean energy (such as wind and solar) and thus play a key role in the increasing global challenges of energy, environment, and climate change.^[1,2] These energy storage technologies have been widely used not only in power electronics (portable, implantable, and electronic devices, such as mobile phones and laptops),^[3–5] but also in electric vehicles.^[6–8]

In recent years, the development of advanced materials, including nanoporous carbons, graphene,^[9] two-dimensional (2D) transition metal carbon/nitride (MXenes, such as Ti₃C₂ and Ti₃N₂),^[10–12] 2D transition metal sulfide (TMSs, such as MoS₂^[13]), and conductive metal-organic frameworks (MOFs) electrodes,^[14] has offered great opportunities to improve the device performance and fill the gap between the current performance and the demand of modern energy storage devices.^[15]

These high promises are derived from the unique advantages these materials offer in terms of superior electronic properties, large accessible surfaces, abundant surfaces and coordination sites, the possibility for multiple oxidations, etc.^[16,17]

Typically, the electrochemical characterization of electrode materials is investigated mainly by conventional electrochemical analytical methods, including cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS), which provide suitable data for assessing the electrode performance but maybe sometimes limited to provide comprehensive information and explanation regarding the dynamic physicochemical behavior of electrodes and electrolytes during the electrochemical processes.^[18] In addition to CV, GCD, and EIS, a series of analytical techniques have been designed in combination with traditional electrochemical methods to achieve the purpose of in situ electrochemical analysis, such as in situ X-ray diffraction (XRD), in situ electrochemical dilatometry, in situ electrochemical quartz crystal microbalance (EQCM), in situ nuclear magnetic resonance (NMR), in situ Raman spectroscopy, in situ quasielastic neutron scattering (QENS), etc.

Among them, in situ XRD, combined with electrochemical dilatometry, is an effective technique to investigate the electrode/electrolyte interfacial structure, as it allows for monitoring the interlayer distance or volumetric change during the electrochemical cycling.^[19,20] In situ X-ray scattering technique can bring information about the pore size and shape, length scale of partially ordered nanoparticle, or nanoporous materials.^[21,22] In situ EQCM experiment in gravimetric mode tracks the ion fluxes in the electrode materials, which is critical to understand the change of ion population under applied potential.^[23,24] In situ NMR is an essential tool to probe the ion configurations and adsorption

structure inside the porous electrodes, providing direct evidence to capture the charging dynamics.^[25,26] Other quantitative spectroscopic analyses, such as in situ/operando Raman spectroscopy, have been developed to explore chemical/physical processes, including the effects of electrochemical doping, electronic state energy, and ion intercalations.^[27] QENS probes the microscopic ion dynamics and long-range translational diffusion under confinement.^[28,29] Moreover, atomic force microscope (AFM) could measure the force during the surface scanning, which could be well coupled with MD simulations.^[30]

With the progress of the fundamental theory of electrochemical energy storage and the development of computational simulation methods as well as computational capabilities, theoretical approaches are increasingly used to explore the energy storage mechanisms of the devices at the nano-/micro-scale. These methods can provide accurate descriptions of the electrode/electrolyte interface at the molecular scale under cycling conditions.^[31,32] The modeling investigation of energy storage devices has led to many research projects, involving a wide range of methods such as fundamental theory,^[33–36] molecular dynamics (MD)^[37] and Monte Carlo (MC) simulations,^[22,38] and density functional theory (DFT).^[43] Such theoretical methods are particularly useful for getting insights into charging mechanisms when combined with in situ experimental techniques.^[20,22,24,40]

This short review aims at covering the latest progress of computational modeling methods and their use combined together with advanced in situ analysis techniques, by relating the examples of works investigating the charge storage mechanisms in some typical nanoscale materials. We will first focus on a few critical aspects of molecular simulations of supercapacitors before focusing on studies of nanoporous materials, including porous carbons, conductive MOF electrodes, and 2D MXene materials. The combination of simulational and experimental approaches can provide a detailed and coherent view of the electrochemical processes occurring at the electrodes and support further development of the next generation of electrochemical capacitor devices.

2. Computational Simulation Techniques

Electrochemical capacitors (ECs, also termed as supercapacitors) store the energy by charge separation at the electrode material/electrolyte interface. Two different types of ECs can be defined, depending on the charge storage mechanism.^[41,42] Materials used in electrochemical double layer capacitors (EDLCs) store charge by electrostatic adsorption of ions at the electrode/electrolyte interface, without any redox reactions. This mechanism makes MD simulations very suitable for studying such systems. Indeed, MD simulations typically include electrostatic and van der Waals interactions between atoms/molecules.^[43] Differently, redox capacitive materials, called pseudocapacitive materials, store charge through fast, non-diffusion limited redox reactions at the near-surface of the material. During the electrochemical process, the charge transfer and potential at the electrode interface are possibly well treated by first-principles calculations based on solving the Schrödinger equation.^[39]

Besides, first-principles molecular dynamics (FPMD, also called *ab initio* molecular dynamics, AIMD) methods^[44] and reactive molecular dynamics methods (using, e.g., the ReaxFF force field)^[29,45] can be efficient to simulate some critical interfacial reactions and interactions during the electrochemical processes. Compared with classical non-reactive force fields, reactive molecular dynamics provide a more accurate prediction of transition states and reaction dynamics, sometimes at the



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chemical principles of supercapacitor systems.



Zifeng Lin received his PhD degree from the Université Paul Sabatier (Toulouse, France) in 2017, under the supervision of Prof. Patrice Simon and Dr Pierre-Louis Taberna. After a year's postdoctoral research training in the same group, he joined Sichuan University (China) in 2018 as a Research Fellow (PI). His research interests are in the area of nanostruc-

tured materials for energy storage devices including electrochemical capacitors and metal ion batteries.



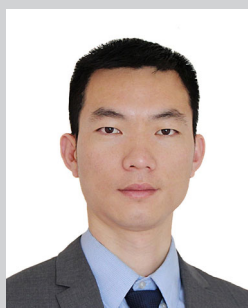
Céline Merlet is a CNRS researcher at Université Paul Sabatier in Toulouse. She received her PhD degree in 2013 from Université Pierre et Marie Curie in Paris where she had worked on molecular simulations of carbon-carbon supercapacitors. She then joined the University of Cambridge as a postdoctoral researcher working on simulating NMR spectra of

ions in energy storage materials such as porous carbons and lithium manganese oxides. Since 2017, she has been working at the CIRIMAT laboratory on the development and application of multi-scale models for a better understanding and performance prediction of electrochemical energy storage systems.



Guang Feng received his PhD degree from Clemson University in 2010. During 2010 to 2013, he worked in Vanderbilt University and The Fluid Interface Reactions, Structures and Transport (FIRST) Energy Frontier Research Center as a postdoctoral research associate and then a research assistant professor. By November 2013, he became a professor in Huazhong University of Science and Technology.

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Jixin Zhu is currently a full Professor at the Institute of Advanced Materials, Nanjing Tech University. In 2012, he received his Ph.D. degree from Nanyang Technological University and then worked as a postdoctoral fellow in TUM CREATE from 2012 to 2014. After that, he moved to Max Planck Institute of Colloids and Interfaces as a postdoctoral fellow.

He was selected as Clarivate Analytics “Highly Cited Researcher.” His research topics mainly include advanced functional materials for energy storage and conversion, flexible electronic device applications.



Patrice Simon is currently a distinguished professor of Materials Sciences at Université Paul Sabatier (Toulouse, France) and serves as Deputy director of the French network on electrochemical energy storage (RS2E). He received his PhD in 1995 from Ecole Nationale Supérieure de Chimie, Toulouse. He was appointed as Assistant Profes-

sor—Chair of Electrochemistry—at Conservatoire National des Arts et Métiers in Paris, and joined Université Paul Sabatier in 2001. His research activities are focused on the modification of material/electrolyte interfaces in electrodes for electrochemical energy storage devices, including batteries and electrochemical capacitors.

price of a long parametrization process. Compared with static quantum calculations, reactive molecular dynamics can simulate the environment surrounding an electrochemical process (such as temperature, pressure, and other external conditions) in a dynamic way, even for relatively large system. Such methods can thus be very suitable for studying the electrochemical events during the charging/discharging of electrochemical energy storage devices.

2.1. Constant potential and constant charge methods

Among the above-listed simulation approaches, classical MD methods have the unique advantage of allowing to apply controllable external potentials conditions, so that real-time simulations can be achieved and directly compared with extensive in situ experimental analysis. A bias voltage can be applied to an EDLC simulation cell, composed of two distant electrodes and an electrolyte in between and inside the porous electrodes (as shown in **Figure 1a**), to simulate the dynamic charging/discharging process through either the constant potential method (CPM) or the constant charge method (CCM), as shown in **Figure 1b**.^[43,46–48] The CPM approach, originally proposed by Siepmann and Sprik,^[49] and further developed by Reed et al.,^[50] considers the electrodes as ideal metals. This means that all atoms of a given electrode are maintained at a constrained equal potential which gives an accurate description of the charge distribution on the electrodes in many cases. This method has been successfully implemented in a variety of simulation softwares, including LAMMPS,^[51] GROMACS,^[52] and MetalWalls.^[53]

The CPM approach allows the charge of the electrode atoms to fluctuate in response to the electrolyte ions and molecules in the vicinity of the electrode surface. On the contrary, the CCM approach considers fixed charges on the electrode atoms, assigned arbitrarily, and very often uniformly. In this case, the potential on each electrode atom is a priori unknown and sometimes hard to calculate.^[54] The CPM approach is thus considered more realistic than the CCM approach, especially in curved carbon nanopores and for studying charging dynamics.^[55] Liu et al.^[56] conducted simulations using the CPM approach with carbon electrode materials, called zeolite templated carbons (ZTCs), which have well-defined pores. Their results show that in a pore with a smaller radius of curvature, the charge compensation per carbon (CCpC), defined as the average charge of the electrode atoms within the coordination shell of a counterion, tends to be higher than in a pore with a larger radius of curvature, as represented in **Figure 1c**. The higher CCpC indicates more efficient charge storage, as counterion charges are better screened, allowing for a larger storage within the electrode. This phenomenon could not be evidenced when conducting a CCM simulation with fixed uniform charges on the electrode atoms. However, with planar surfaces, as in the case of graphene/graphite surface, the CCM method could result in credible EDL structures and capacitive results, comparable with the CPM simulation.^[47]

An important drawback of CPM simulation is that they are computationally much more expensive (by at least an order of magnitude), not only in CPU resources but also in memory resources. The charges on the electrode atoms, which need to be calculated at each time step, can be evaluated using 1) a conjugate gradient method, the slowest option, or 2) using an initial matrix inversion (done once at the beginning of the simulation) followed by a matrix multiplication (at each time step), the fastest option. The second case can unfortunately be applied only if

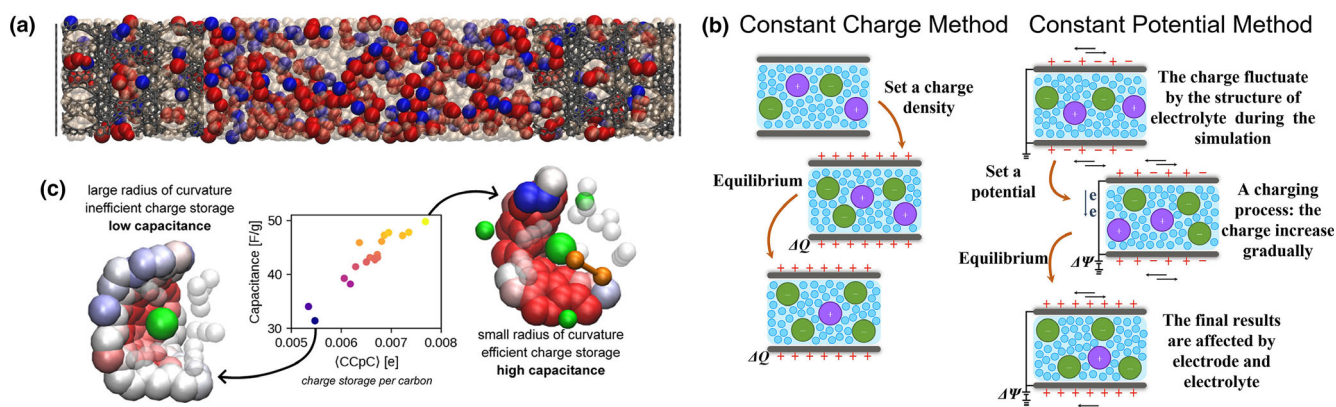


Figure 1. a) A common simulation setup for EDL capacitors, the electrode on each side can be graphene, porous carbon, or MXene material, etc., the electrolytes can be aqueous, organic or neat ionic liquid. Reproduced with permission.^[56] Copyright 2019, American Chemical Society. b) Schematic diagram of the simulation process and electrode charge evolution with CCM and CPM. Reproduced with permission.^[47] Copyright 2017, Wiley. c) Snapshots of charge compensation per carbon (CCpC) of carbon pore with large and small radii. The carbon atom of the pore is colored according to their induced charge, with red indicating positive and blue indicating negative, scaled from -0.01 to 0.01 e.

electrode atoms are immobile along the entire trajectory. When starting at zero voltage or zero charge and setting a specified potential value, the charges on the electrode atoms evolve gradually until equilibrium, which always needs a long simulation time. A feasible strategy to shorten the equilibration time is to apply first a constant charge during an appropriate time before applying a constant potential as proposed by Merlet et al.^[46] Such an equilibration approach is needed to be done carefully due to the difficulty of assessing the constant potential to apply in the CPM simulations.^[51,56]

Since the CPM simulation assumes that electrodes are ideal metals with all atoms being equivalent, it works quite well with homogeneous pure carbon electrodes. In this case, the charge on each carbon atom depends only on the potential applied and the surrounding electrolyte ions, because it is zero in the neutral state. However, the CPM approach fails short to describe materials with several types of atoms, for example, multi-layer MXene materials. For MXene electrodes, the charge on the electrode atom depends on the nature of the atom (C, Ti, O, F, and H), the potential applied, and the surrounding electrolyte. When using the CPM approach on a MXene electrode, all atom charges are treated in the same way, whatever the chemical nature of the atom. **Figure 2a** shows the distribution of charges obtained for a CPM simulation done at constant 0 V potential with a $\text{Ti}_3\text{C}_2\text{O}_2$ MXene material in contact with 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMIM-OTF). It leads to small (-0.1 e $< q < 0.1$ e) but non-negligible charges on the surface atoms and negligible charges for the inner atoms. While various experimental^[57,58] and DFT theoretical studies^[39,59,60] propose somewhat different atomic charges on the MXene materials, all these studies show that atomic charges for different atoms (C, Ti, O, F, and H) are much higher than the ones calculated using the CPM simulation, as represented in Figure 2b.

Following the wrong charge distributions obtained with the CPM approach and the fact that XANES and Electron energy loss spectroscopy (EELS) experimental results show that the oxidation state of MXene atoms only changes weakly upon charging,^[39,57,61] it would be suitable to conduct CCM simulation with MXene electrodes using the DFT calculated atomic charge distributions. Such CCM simulations have been recently successfully applied to MXene based system to study the

influence of the solvent^[60] and room temperature ionic liquid (RTIL)^[62] on charge storage.

Ideally, simulations should be done assuming a constant potential with a representation of the semi-conducting character of MXenes and including distinct behaviors for the various atom types. While a recent work focuses on tuning the metallicity of electrodes,^[63] showing a strong effect on structural and capacitive properties, a method including both this effect and distinct behaviors for the various atom types does not exist yet and should be an important and urgent research topic.

2.2. Advanced simulation techniques

In addition to the mature theoretical calculation methods discussed above, the exploration of new advanced computational techniques is also in progress. Novel simulation methods are proposed to predict capacitances more accurately, speed-up the screening of materials, or solve some limitations of traditional methods. The lattice model developed by Merlet et al.^[64] and the lattice Boltzmann electrokinetics approach proposed by Asta et al.^[65] are examples of such innovative simulation methods. More recently, Belhoub et al.^[66] reported a mesoscopic lattice model, which can predict dynamical, structural, and capacitive properties for EDLC. Most notably, this method is 10,000 times faster than the other conventional molecular simulations while keeping an ability to predict capacitances and quantities of adsorbed ions in good agreement with experimental results.

On a more local scale, beyond the conventional *ab initio* or reactive force field MD simulations investigating the electron transfer at the electrode/electrolyte interface, Jeanmairet et al. presented an alternative method, named as molecular density functional theory (MDFT).^[67,68] This MDFT could be used to investigate electron transfer reactions in aqueous electrolytes, while retaining the molecular description of the solvent, at a much faster computational speed than traditional methods. The MDFT method can be used to compute the average vertical energy gap, relevant reaction coordinate, reorganization free energies, and free energy curves of a specific system.

Based on the finite field method and constant potential approach, Dufils et al.^[69] proposed a more efficient way of simulating an electrochemical system, which can be easily applied to both classical and ab initio molecular dynamics simulations. In this method, a single solid is used to simulate both negative and positive electrodes. With this way of simulating electrochemical systems, the gap between simulations at different scales is reduced and it becomes possible to simulate directly the electrochemical reactions at the electrodes/electrolyte interface with first-principles simulations.

3. Insights into Nanoporous Electrodes

Nanoporous carbons are by far the most widely studied class of materials in the field of computational studies of supercapacitors. While these systems appear simple, a deep understanding of the structure–property relationships and the ability to predict accurately the performance of such EDL capacitors are still lacking. MOFs are a new class of materials which show potential in energy storage applications. Left aside for a long time because of poor conductivities, they are now showing promising properties.

3.1. Ion arrangement in carbon nanopore

Using computational simulation methods, it is now possible to get a better understanding of charge storage mechanisms under nanoconfinement, which is a crucial topic in designing high energy density and high-power density supercapacitor devices. Thanks to their wide variability of morphologies and relatively simple chemical nature, nanoporous carbons are ideal materials in that aim.^[70] To investigate well-characterized carbide-derived carbons (CDC) and the typical RTILs EMIM-TFSI (1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide) and EMIM-BF₄ (1-ethyl-3-methylimidazolium tetrafluoroborate), Futamura et al.^[21] employed MC simulations combined

with X-ray scattering experiments. They found that ions adopt a single layer or bilayer arrangement depending on the average pore size when confined in carbon nanopores (Figure 3). When EMIM-TFSI ions are confined in 0.7 nm diameter pores, a monolayer with a partial breaking of the coulombic ordering can be observed. The repulsive electrostatic interactions between co-ions being screened by image charges created on the carbon, non-Coulombic ordering can be achieved where confined co-ions get closer to each other, compared to the bulk electrolyte. The non-Coulombic ordering, observed in this case in unpolarized carbons, could be further enhanced under applied external electric potential. This work experimentally validates the theoretically predicted “superionic” state by Kornyshev et al.,^[36] which is exactly proposing that ions of like charge can be in close proximity in nanopores where the charge screening by the electrodes is important. Furthermore, this phenomenon gives an atomic scale explanation to the experimentally discovered increase of capacitance when the average pore size matches the ions dimensions in an RTIL/carbon system.^[71] Indeed, such an effect will facilitate charge separation, that is, separation of counterions and co-ions, leading to an increase of electrolyte charge in the electrodes, compensated by the electrode charge and thus providing higher capacitances.

3.2. Ion dynamics in carbon nanopore

Ion dynamic and electroadsorption kinetics under confinement is another key aspect, which directly affects the power density of the energy storage devices. Mo et al.^[52] performed CPM MD simulations to investigate the charging dynamics of slit-shaped subnanometer carbon pores with ionic liquids. Their simulation results revealed that the charging dynamics of the ions exhibit a non-monotonic relation between the pore size and the charging rate. Especially, the charging process is significantly boosted in subnanometer pores with sizes of 0.45 and 0.75 nm, defying conventional belief that small pore size results in slow charging rate.^[72] Their analysis uncovered that the mechanism of such

anomalous enhancement of the charging dynamics could be attributed to a structural transition of in-pore ions. Some layer arrangements will facilitate the ion transport from layer to layer and accelerate the ion diffusion along the pore length direction. In very small pores, the charging dynamics can be particularly hindered, as was demonstrated by Breitsprecher et al.^[73] who propose a way to increase the speed of charging in such case by rising the potential slowly rather than in one step.

Liu et al.^[56] have shown that in more complex but regular carbon structures, the charging time is correlated with the pore limiting diameter. In that study as well, the correlation is not monotonic suggesting that specific ion arrangements will be more

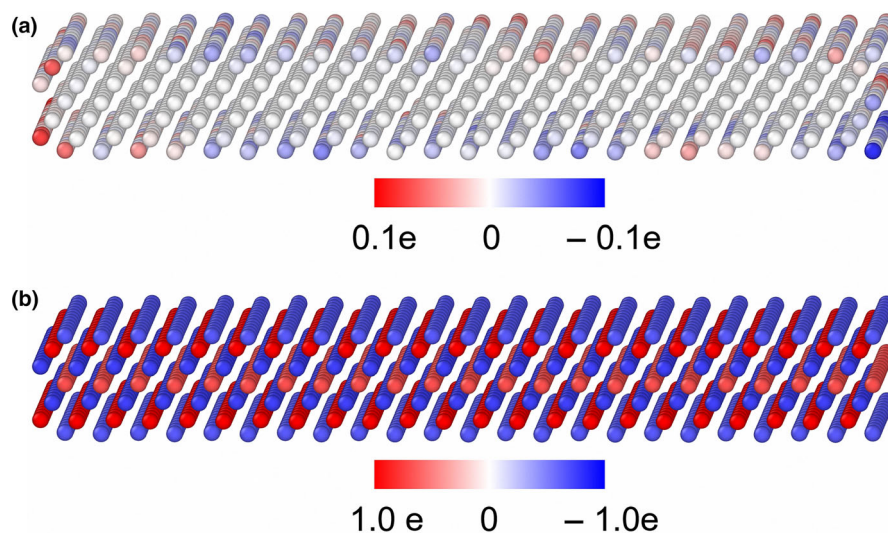


Figure 2. Atomic charges on Ti₃C₂O₂ MXene electrodes in contact with EMIM-OTF a) calculated using CPM at 0 V, b) calculated using DFT. The atoms are colored according to their induced charge, with red indicating positive and blue indicating negative, scaled from -0.1 to 0.1 e and -1.0 to 1.0 e, respectively.

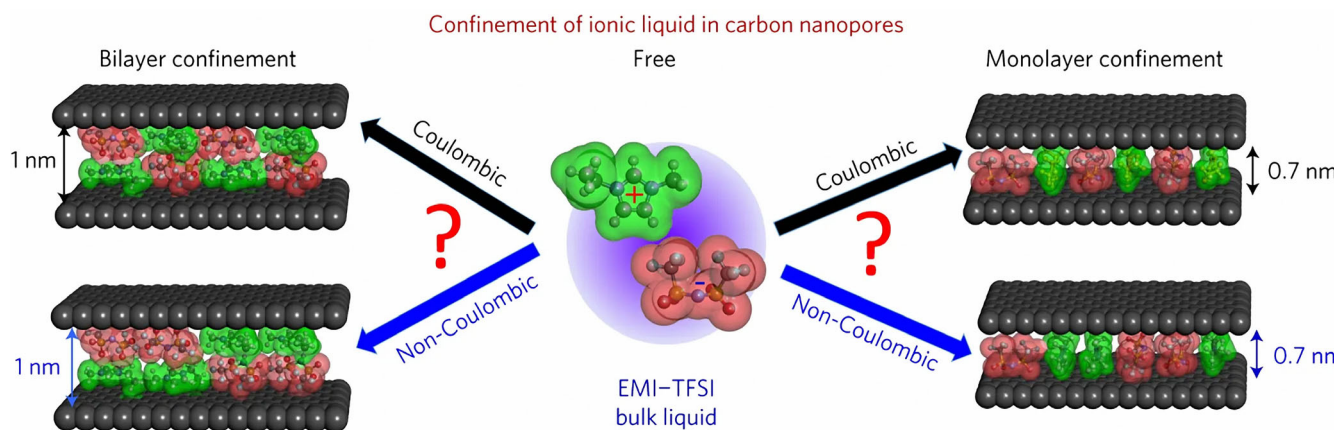


Figure 3. Schematic representation of the structure of EMIM-TFSI confined in nanoporous carbon pores with or without Coulombic ordering. Reproduced with permission.^[21] Copyright 2017, Nature Publishing Group.

favorable than others although it is worth noting that a single pore size is sufficient to describe slit pores while it is not the case for 3D structures with interconnected pores. Indeed, MD simulations have shown that charging dynamics in disordered porous carbons are heterogeneous.^[74]

Whichever type of nanoporous material is studied in simulations, the timescales and length scales are always reduced in these microscopic models compared to experiments. One common way to link the simulation results with experiments is the transmission line model (TLM) applied successfully in a number of studies.^[74–76] For large potentials, the transmission line model is not directly applicable anymore and more complex models need to be developed.^[77]

3.3. Interpore ionic interaction effect

In most works dealing with charge storage mechanisms in porous carbons, single nanopores are studied and considered as representative of porous networks. However, in realistic porous carbons, there are always tens of pore in close contact, so that the effect of interpore, across carbon, ion–ion correlations should also be taken into account. Mendez-Morales et al. have studied ion–ion correlations across and between electrified graphene layers using MD simulations.^[78] They have shown that under strong confinement, due to highly localized image charges, ions of the same charge tend to adsorb in front of each other across the graphene plane. More recently, Kondrat et al.^[79] developed a lattice model to study the interpore ionic interactions and pore-wall transparency on charging nanoporous electrodes. By combining MC simulations, mean-field theory, and perturbation analysis, they proposed that interpore interactions could enhance or hamper the stored charge density, depending on the sign of the interactions. In addition, their simulation results predict that the charging could proceed either via a phase transition or continuously, and suggest that tuning the interpore ion–ion electrostatic response and thickness of pore walls would be promising for optimizing the design of supercapacitor.

3.4. Ion arrangement and dynamics in MOFs pores

Conductive MOFs are another class of promising nanoporous electrodes, thanks to their high surface area far exceeding that of

conventional porous carbons, their high compressibility, and their tunable structure. The main drawback comes from their limited electrical conductivity. Sheberla et al.^[80] reported that the $\text{Ni}_3(\text{HITP})_2$ MOF could reach $\sim 5000 \text{ S m}^{-1}$ bulk electrical conductivity, far exceeding holey graphite and activated carbons, $\sim 1000 \text{ S m}^{-1}$. The enhanced electrical conductivity allows $\text{Ni}_3(\text{HITP})_2$ MOF to be used as an electrode material in EDLC with a high specific capacitance ($\sim 18 \text{ } \mu\text{F cm}^{-2}$).^[14] Following this initial experimental work, Bi et al.^[81] performed MD simulations with the CPM approach and presented an atomic understanding of the capacitive performance and double-layer structure of EDLC composed of Conductive MOFs and RTIL. Their MD simulation model is presented in **Figure 4a**, where two $\text{Ni}_3(\text{HITP})_2$ MOF electrodes with honeycomb structures (schematically shown in Figure 4b) are immersed in EMIM- BF_4 electrolyte. The in-pore charge and ion density distributions at neutral and polarized MOFs with different pore sizes were calculated. The in-plane averaged 2D maps of charge distributions of EMIM- BF_4 inside pores of the $\text{Ni}_3(\text{HITP})_2$ MOF, at -2 , 0 , and 2 V , are shown in Figure 4c, as an example. At the neutral state, the ions form a layer adsorbed near the pore surface and organize following a hexagonal pattern in the plane section. Under polarization, the counterions separate and stay between the central-line and surface adsorbed layer, while the co-ions are located between those two regions.

In terms of capacitive performance, the simulation results predicted that the $\text{Ni}_3(\text{HITP})_2$ MOF could deliver a capacitance of $\sim 9 \text{ } \mu\text{F cm}^{-2}$, which is comparable with reported RTIL based porous carbon EDLCs. The charging dynamics are well described by a TLM. The fitting results show that the conductivity of the ionic liquid in the pores is much lower than that in bulk state. Therefore, it can be considered that the impedance response of the EDLC based on conductive MOFs and ionic liquid is mainly determined by the transport of ions in the pores. The combined nanoscale-to-macroscale investigation demonstrates the potential of conductive MOF for supercapacitors applications, despite the fact that the energy density has to be improved.

4. Insights into 2D Layered MXene Materials

2D transition metal carbides and nitrides, also known as MXenes, are one typical representative of transition metal-based low-dimensional

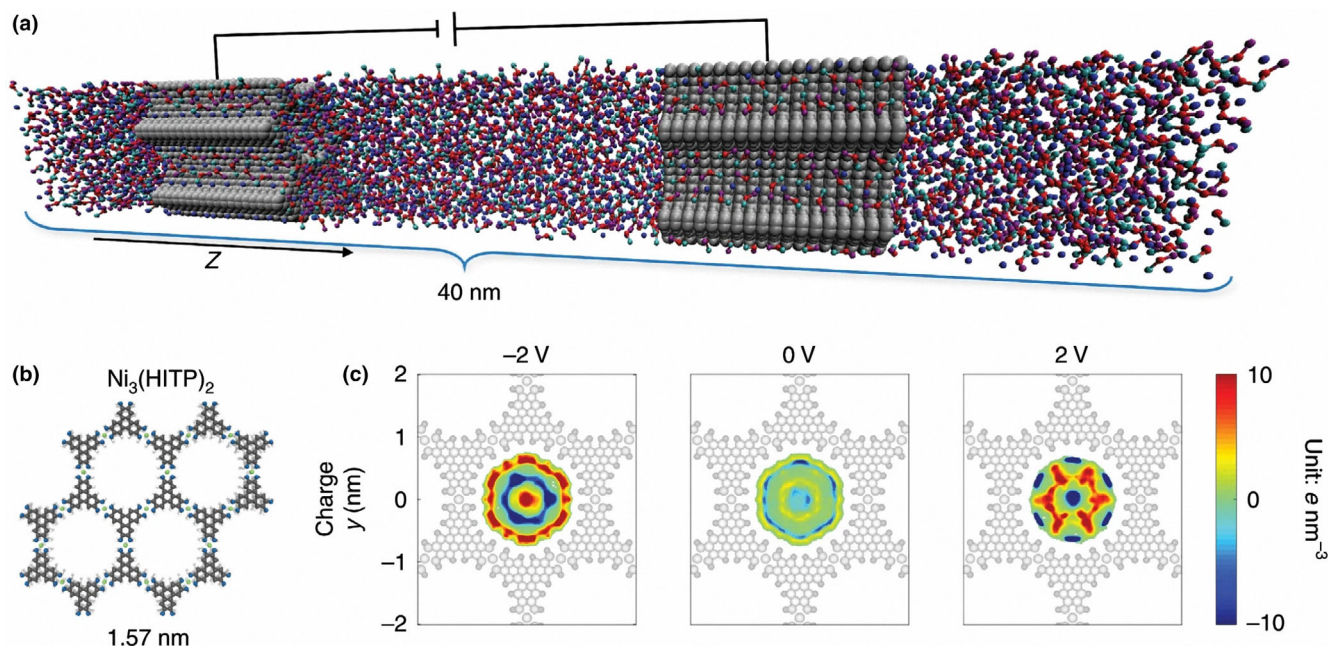


Figure 4. a) Schematic of the MD simulated supercapacitor with MOF as the electrodes and RTIL EMIM-BF₄ as electrolyte. b) Schematic of 2D honeycomb structures of studied Ni₃(HITP)₂ MOF sheets, with 1.57 nm effective pore diameters. c) In-plane averaged 2D maps of charge distributions of EMIM-BF₄ inside pores of a studied Ni₃(HITP)₂ MOF. Reproduced with permission.^[81] Copyright 2020, Nature Publishing Group.

systems, and have been extensively studied as electrode materials for energy storage applications,^[10] due to their intrinsic layered structure, surfaces rich in functional groups, and multiple oxidation states. To get a better understanding of the complex charge storage mechanisms in these materials, many works have been made using a large variety of advanced techniques in recent years. The following section reviews the latest advances on the study of charge storage mechanisms in MXenes in different electrolytes.

4.1. Aqueous electrolytes

Combining DFT calculations and in situ XRD, Mu et al.^[82] investigated the charge storage mechanism of Ti₃C₂T_x MXene in 1 M H₂SO₄ aqueous electrolyte. They found that the charge storage mechanism in H₂SO₄ solution could be divided into three stages: 1) electrochemical double layer mechanism with no significant lattice parameter change of the MXene structure between -0.25 and 0 V (vs Ag); 2) below -0.25 V, proton insertion between the layers along with electrostatic shrinking, and redox reaction beginning to convert some =O groups to -OH groups. 3) below -0.5 V, second redox reaction upon further proton insertion converting more =O groups to -OH groups, and the *c* lattice parameter increasing due to like charges being repelled from the formed -OH terminated surface groups. The conversion of =O to -OH causes a change of the oxidation state of Ti from $+2.33$ to $+2.43$, confirmed by electrochemical in situ X-ray absorption spectroscopy measurements.^[57]

Considering the critical role of intercalated protons in the redox reaction, Sun et al.^[44] further investigated the pseudocapacitive charge storage mechanism of MXene in H₂SO₄ electrolyte using FPMD simulations. They show that proton redox and transfer

processes could reversibly occur between interfacial water molecules and =O surface sites, accompanied by a more frequent in-water proton transfer. In highly confined water monolayer (between the MXene layers), the surface redox reaction exhibits higher rate than in two or three layers of water. The proton transfer mobility increases linearly with the number of water layers and approaches the bulk state in three-layer water. The authors further propose that the intercalated proton transfer through the MXene edge, from the bulk electrolyte to the MXene redox-active site in the inner layer, could be the bottleneck of the ionic transport. By comparing pristine Ti₃C₂T_x MXenes (termed as P-MXene) and Ti₃C₂T_x MXenes after annealing treatment at 500 °C (termed as 500-MXene), Shao et al.^[83] revealed that the presence of confined water molecules inside the MXene layers dramatically affects their pseudocapacitive behavior, by providing proton transport pathways which activates the redox reaction on the Ti atoms. Their MD simulations show that inside the 500-MXene layer, water molecules could form a better organized and more compact monolayer, as shown in **Figure 5b, d, g**, compared with P-MXene (**Figure 5a, c, e**). The well-organized hydrogen bond network would favor a rapid proton transfer during the electrochemical process. The probability distributions of water molecular dipole orientation inside P-MXene and 500-MXene layers (**Figure 5f**) proves that reducing the content of -OH existing on the outermost surface could lead to a flatter orientation of confined water molecules, thus enhancing the hydrogen bond network. Using a combined in situ Raman spectroscopy analysis, Hu et al.^[27] demonstrated that hydronium is involved in bonding with =O during cathodic polarization (discharging), while debonding happens upon oxidation (charging). This reversible bonding/debonding on the surface functional group leads to a change of the valence state

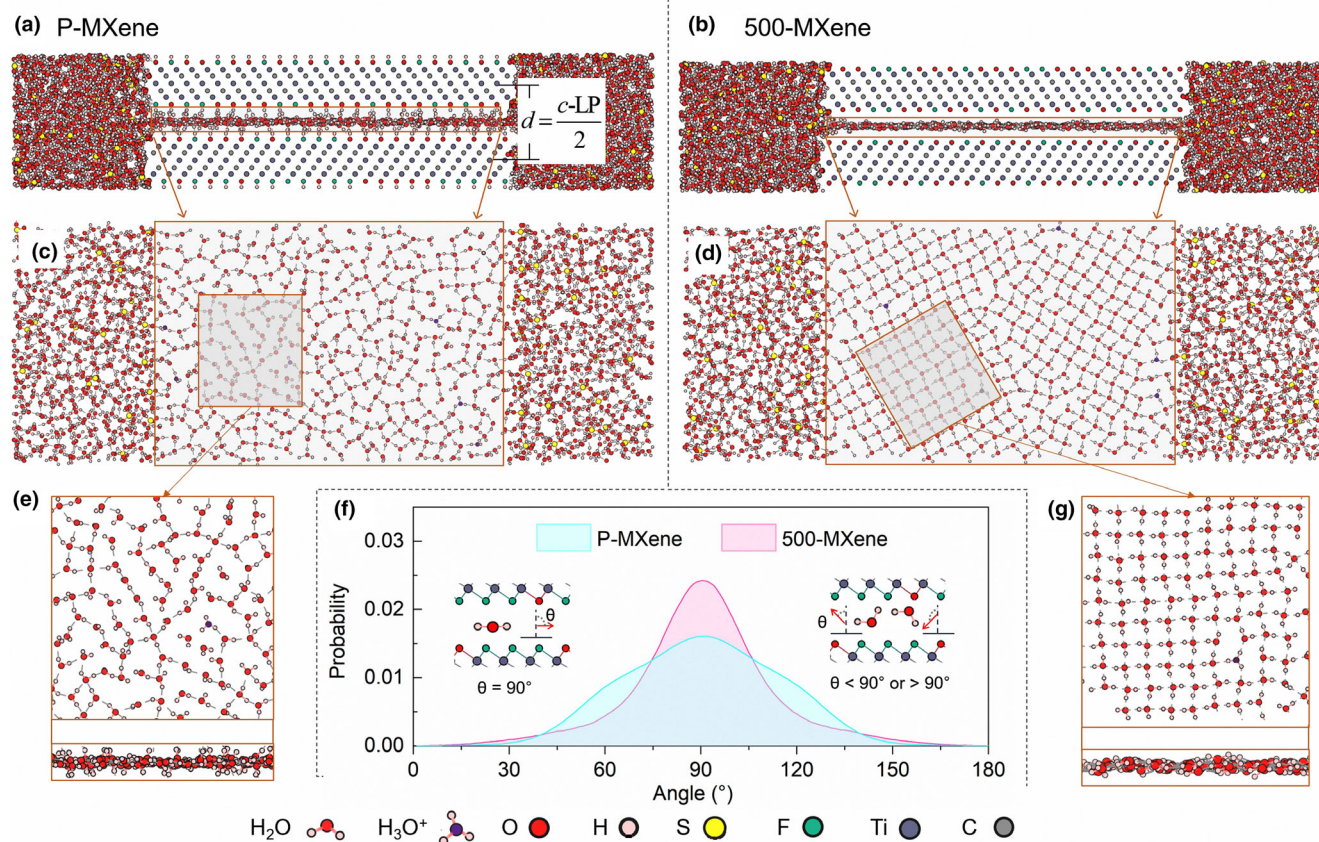


Figure 5. Side view of P-MXene a) and 500-MXene b) layers with monolayer intercalated molecules. Top view of the intercalated molecules between the P-MXene c) and 500-MXene d) layers. Close-up side view and top view of the intercalated water distribution inside the P-MXene e) and 500-MXene g) layers. f) Probability distributions of water molecular dipole orientation inside P-MXene and 500-MXene layers. Reproduced with permission.^[83] Copyright 2020, American Chemical Society.

of Ti atom, which explained the pseudocapacitive mechanism in the acidic electrolyte.

4.2. Intercalation of various cations

A number of studies have been conducted to unravel the effect of using different metal cations on the charge storage mechanism. To this aim, Osti et al.^[29] combined QENS, SANS, and XRD experiments, with MD simulations using the ReaxFF force field. The diffusion coefficient of water confined inside the interlayer gap was found to be about half of the bulk water one. When K^+ ions are intercalated into MXene layers, larger and/or more ordered crystalline domains are formed, and the MXene layers turn out to be more uniform and homogeneous, as presented in **Figure 6a**. The intercalated metal cations reduce the strength of hydrogen bonding between the intercalated water and enhance the ordering of water molecules. These more stable and less mobile water molecules in K^+ -intercalated MXene could increase the stability of the 2D layered material thus limiting structural change under operating conditions. The ordering of water molecules increases with the size of the metal ions (e.g., Li^+ , Na^+ , and K^+). Using Na^+ as intercalated metal ion (from sodium acetate and sodium hydroxide), authors showed that the water dynamics are only weakly affected.^[45] Employing NMR and

DFT calculation, Kajiyama et al.^[84] revealed that $Ti_3C_2T_x$ MXene in non-aqueous Na^+ -containing electrolyte (1 M $NaPF_6$ in ethylene carbonate/diethyl carbonate) suffers from an expansion during the first sodiation, the interlayer distance being further maintained at a constant value. The reversible Na^+ intercalation/deintercalation into the MXene layer without substantial structural change could be due to the pillaring effect of trapped Na^+ and solvent molecules between the $Ti_3C_2T_x$ layers, as shown in **Figure 6b, c**.

4.3. RTIL electrolytes

The charging mechanism of MXene was found to be different in RTIL. Using EMIM-TFSI as the electrolyte, Lin et al.^[20] observed an ideal capacitive behavior within a potential range of -1.5 to 1.5 V, accompanied by an increase of the interlayer spacing upon negative polarization and a slightly decrease upon positive polarization. A similar volumetric change using the same electrode/electrolyte system was also obtained by Jäckel et al.^[85] with in situ electrochemical dilatometry. Still using the same systems, Xu et al.^[62] used an electrode free-moving MD simulation approach with constant charging/discharging conditions. They could propose a description of the charging/discharging mechanism at both positive and negative electrodes that

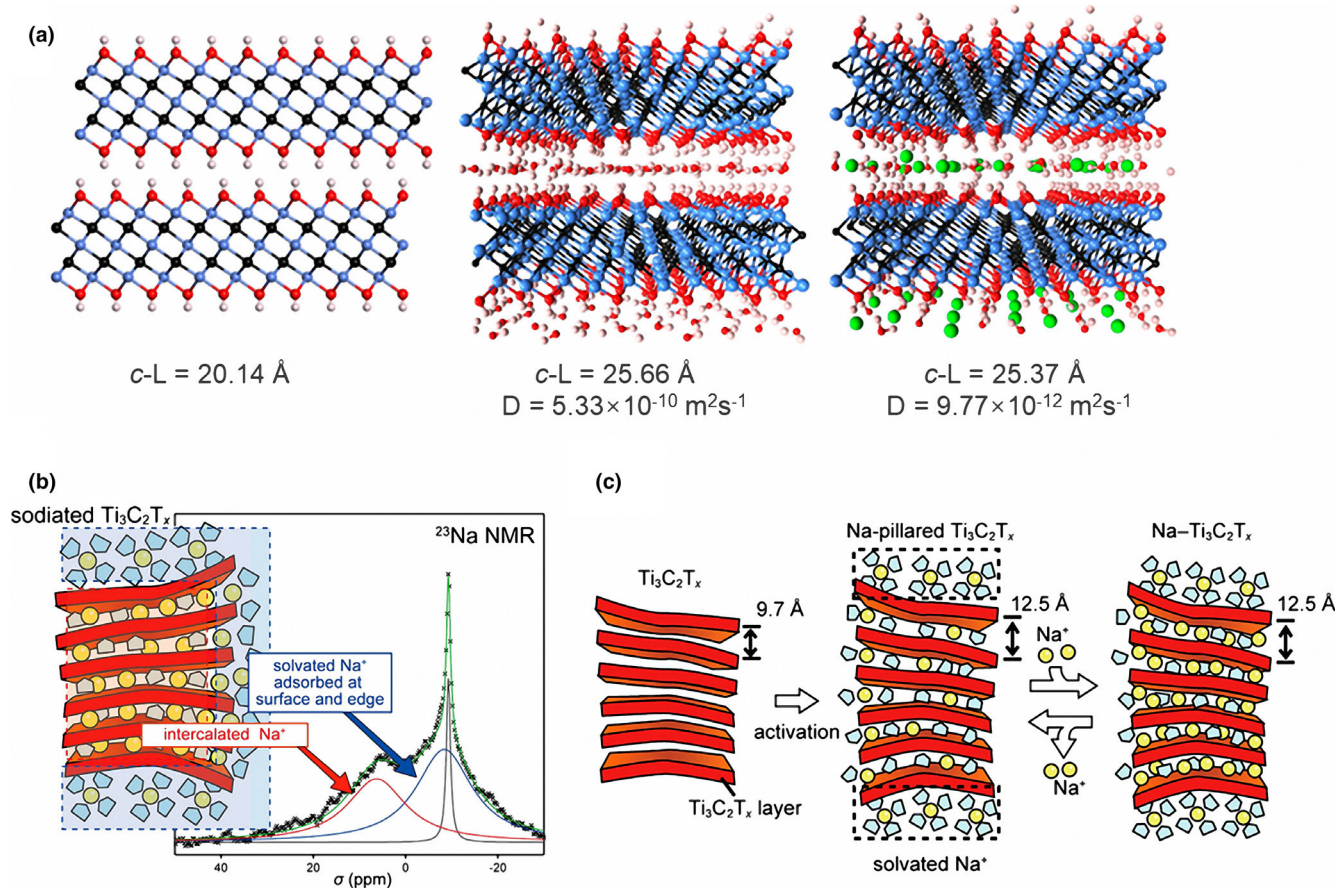


Figure 6. a) Snapshots of MD simulations of the $\text{Ti}_3\text{C}_2(\text{OH})_2$ MXene system with no water, with a single layer of water and K^+ intercalated with a single layer of water, respectively, conducted using the ReaxFF force field. Reproduced with permission.^[29] Copyright 2016, American Chemical Society. The c lattice parameters and diffusion coefficients of water are given. b) ^{23}Na NMR signals used to identify two kinds of Na insertion mechanisms, as shown in the schematic illustration. c) Schematic illustration of the mechanism for Na^+ insertion into the $\text{Ti}_3\text{C}_2\text{T}_x$, accompanied by a c lattice parameter change. Reproduced with permission.^[84] Copyright 2016, American Chemical Society.

nicely fit the experimentally measured electrode volumetric changes. At the positive electrode, the charge storage is mainly achieved by an ion-exchange (counterion intercalation and co-ion deintercalation) process, whereas a counterion intercalation process is observed at the negative electrode.

4.4. Solvent effect in organic electrolytes

The nature of the electrolyte solvents has a critical impact on both the ion dynamics and electrochemical behavior of MXene electrodes. Combining in situ XRD measurements and MD simulations, Wang et al. investigated the change in the charge storage mechanisms with different solvent in organic electrolytes (LiTFSI salt dissolved in ACN/DMSO/PC) with Ti_3C_2 MXene electrodes. They showed that the solvent affects ion transport and intercalation, and drives the charge storage mechanism.^[60] As shown in **Figure 7**, with PC solvent, a complete ion desolvation is observed when Li^+ is intercalated in Ti_3C_2 MXene layer, which results in fast charge transport and high capacity. Interestingly, a similar desolvated Li^+ intercalation was also suggested

in Ti_3C_2 electrode prepared from a molten salt method.^[86] This mechanism is similar to the capacitance increase reported in carbon nanopores.^[87] When using DMSO as solvent, a fast ion transport is observed through the tunnel-like structure, associated with a moderate capacitance. For the ACN solvent, ACN molecules tend to align parallel to the Ti_3C_2 surfaces, which severely hinders the mobility of lithium ions, resulting in the lowest capacitance.

5. Conclusion and Perspective

Understanding the intrinsic characteristics of the electrode/electrolyte interface and the various physicochemical changes occurring during the process of charging and discharging is the main focus of current theoretical calculations and experimental investigations on electrochemical energy storage systems. Although a series of theoretical and experimental methods have been developed, there are still a lot of critical technical challenges and underlying scientific problems to reveal the electrochemical energy storage mechanisms of advanced nanoscale low-dimensional materials.

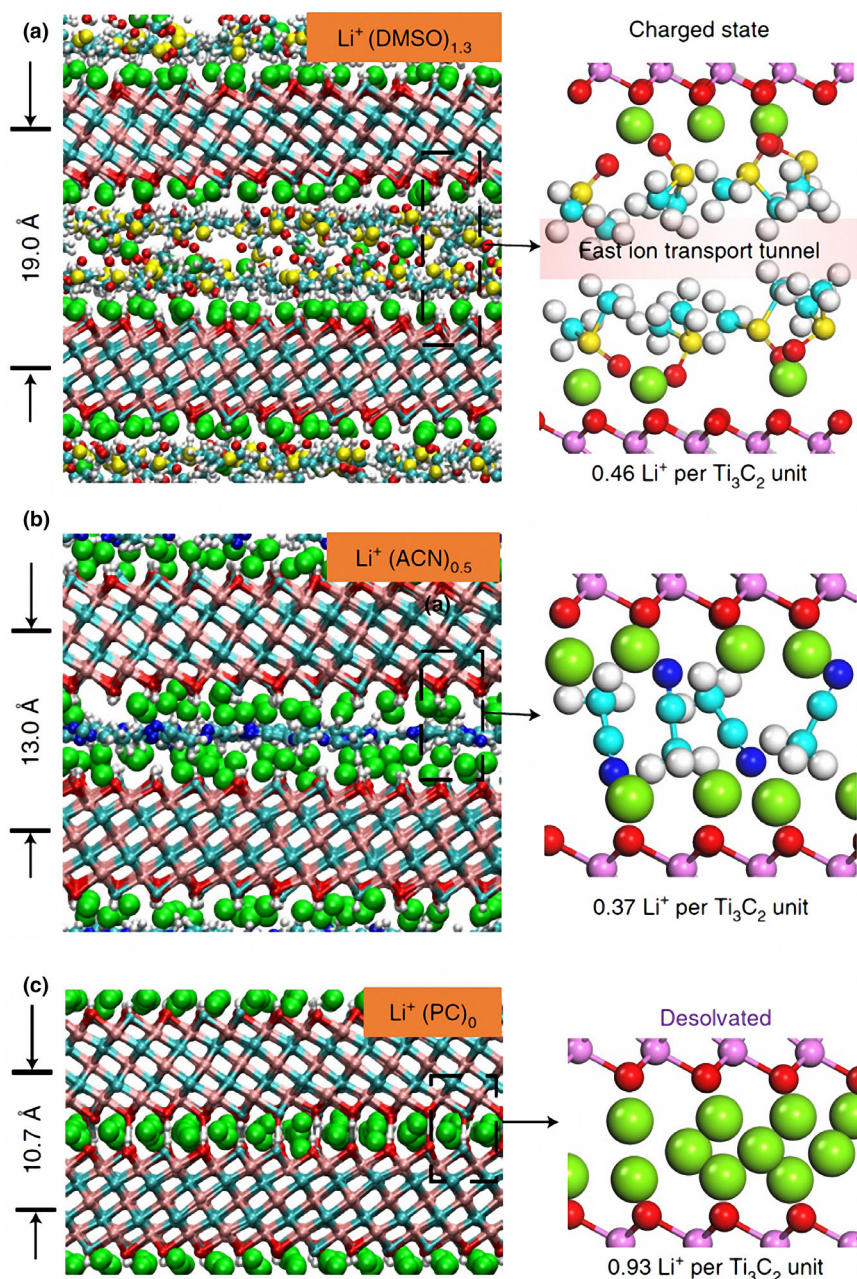


Figure 7. a) Snapshots of MD simulation for DMSO-based electrolyte, indicating a fast ion transport in the tunnel formed inside the MXene and DMSO layer, b) Snapshots for ACN-based electrolyte, c) Snapshots for PC-based electrolyte, indicating a total desolvation on Li⁺ inside the MXene layer. Reproduced with permission.^[60] Copyright 2019, Nature Publishing Group.

One critical challenge across all systems is to reduce the gap between theoretical and experimental studies. This gap corresponds to two main issues: on the one hand, simulation methods are sometimes not realistic enough in particular for the calculation of forces and electronic properties; on the other hand, the length and time scales of simulations are much smaller than in typical experimental setups. In addition, the accuracy of the models usually decreases when larger systems are explored, due to computational cost, such

that a compromise is always necessary. Both MD and DFT calculations are based, to some extent, on simplification and assumptions. For MD simulations, developing polarizable or reactive force fields, which requires parametrization and validation, remains an ongoing challenge in particular for complex interfacial systems with a multitude of atom types. For DFT calculations, the generalized gradient approximation (GGA) functionals, commonly used in describing energy materials, cannot effectively capture the weak non-covalent interactions, which is a crucial part of interfacial interactions. With the progress in computer hardware and molecular simulation methods, this gap is decreasing. At the same time, more performant computers also allow for studying larger systems, but the number of atoms simulated is still limited to around 100,000 for most MD studies and to below 1,000 for DFT. This inevitable simplification of the system and in particular the material structure reduces the accuracy of the model. While slit-shaped, cylindrical, or spherical pores can account for many effects, bridging the time and length scales between theoretical and experimental studies is sometimes necessary, for example, for fine interpretation of in situ experimental results. Methods like molecular DFT and lattice models are being developed to reduce this gap.

In the development and design of the next-generation electrochemical energy storage devices, some key scientific points (non-exhaustive) need to be explored with combined theoretical calculation methods and in situ advanced analytical techniques are as follows:

- 1 The real-time dynamics of nano-confined electrolyte ions during the process of charging and discharging in the electrode materials with characteristic internal morphology (irregular nanopores, 2D layered pores, etc.). Such migration/diffusion characteristics are directly related to the power characteristics of the energy storage device, which is the key to the design of high-power energy storage device.

- 2 The spatial distribution of ions/atoms and charges at the electrode/electrolyte interface, the electronic interaction between the electrolyte, the surface-active sites of the electrode material, and their relationship with the surface potential. Those effects are directly related to the energy storage mechanism and energy storage capacity of the electrode/electrolyte interface, which is the key to the design of high-energy density energy storage devices.

3 The change of structural parameters of electrode materials during the electrochemical charging and discharging process, such as the change of layer spacing of 2D materials, the change of pore diameter in porous materials, and the change of internal electronic structure characteristics of composite electrode materials. The change of geometric structural parameters and internal electronic structure of electrode materials are directly related to the structure/conduction cycling stability of electrode materials, which is the key to design electrode materials with high conductivity and stability.

From the point of view of molecular simulations, developing a tool for constant potential calculations, which would include both structural effect and distinct behaviors for the various atom types, is an essential and urgent research topic. Besides, the gap between simulations at different scales is decreasing, and directly simulating the electrochemical reactions at the electrode/electrolyte interface with first-principles simulation could be possible in the near future.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

2D material, charge storage mechanism, molecular simulations, porous electrode, supercapacitor

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