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Metal–Organic Framework Supercapacitors: Challenges and Opportunities

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Supercapacitors offer superior energy storage capabilities than traditional capacitors, making them useful for applications such as electric vehicles and rapid large-scale energy storage. The energy storage performance of these devices relies on electrical double-layer capacitance and/or pseudocapacitance from rapid reversible redox reactions. Metal–organic frameworks (MOFs) have recently emerged as a new class of electrode materials with promising supercapacitor performances and capacitances that exceed those of traditional materials. However, the comparison of the supercapacitor performance of a porous carbon and a state-of-the-art MOF highlights a number of challenges for MOF supercapacitors, including low potential windows, limited cycle lifetimes, and poor rate performances. It is proposed that the well-defined and tuneable chemical structures of MOFs present a number of avenues for improving supercapacitor performance. Recent experimental and theoretical work on charging mechanisms in MOF-based supercapacitors is also discussed, and it is found that there is a need for more studies that elucidate the charge storage and degradation mechanisms. Ultimately, a deeper understanding will lead to design principles for realizing improved supercapacitor energy storage devices.

1. Introduction

Clean energy storage technologies are critical to transform the fossil fuel-based transportation sector and to store energy from intermittent renewable sources. Supercapacitors have gained much attention due to their fast charging and discharging times, and their long cycle lifetimes.[1] These electrochemical devices usually consist of two solid electrodes, an ion-permeable separator, and a liquid electrolyte. Electrode materials for supercapacitors should have high electrical conductivity, high surface areas for charge storage, and high electrochemical stability. The most widely used electrode materials are porous carbons.[2] They not only fulfil these three conditions but are also cheap, with various synthetic approaches developed to give a range of different structures. However, the structures of porous carbons are challenging to characterize and control, and there are limited approaches to introduce specific new chemical functionalities.[3–8] The disordered nature of porous carbons has also led to seemingly contradictory structure–performance studies,[9] with some studies finding that the capacitance is maximized when the pore size matches the desolvated electrolyte ion size,[3,4,8,10–13] and other studies finding no such correlation.[5,7,14,15]

Hybrid organic–inorganic solids offer potential for functionalizing material properties for a wide range of clean energy technologies. In particular, the high crystallinity and permanent porosity of metal–organic frameworks (MOFs) are attractive, which has led to their study in research applications such as molecule sieving membranes, gas storage, photocatalysis, and photovoltaics.[16] While most MOFs are wide bandgap electrical insulators, more recently electronically conductive and redox-active MOFs have been developed and employed in electrochemical systems, including supercapacitors, batteries, and electrocatalysts.[17–20] Research in MOF-based supercapacitors has significantly increased since an initial report in 2017 that employed $Ni_3(HITP)_2$ (HITP = 2,3,6,7,10,11-hexaiminotriphenylene) as the sole electrode material in a supercapacitor.[21]

In this perspective, we summarize the progress of supercapacitors employing MOF-based electrodes. We first classify

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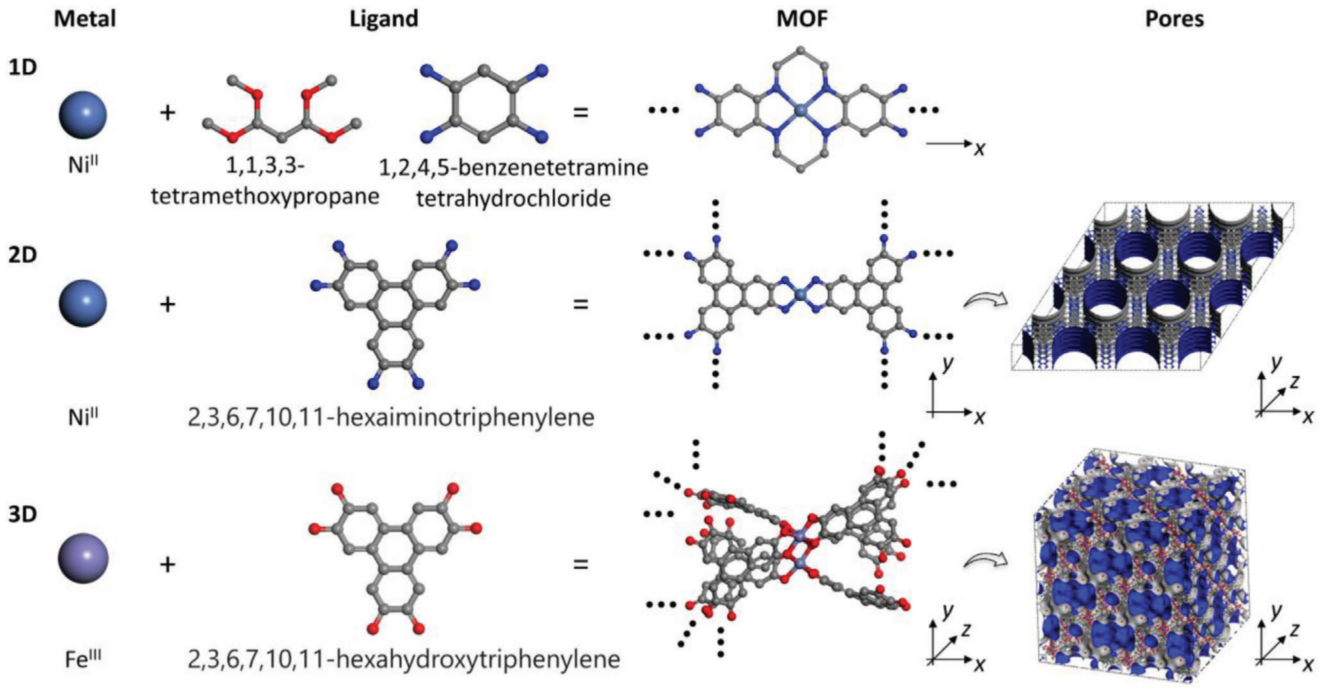

Figure 1. Design strategies for metal–organic frameworks (MOFs) depending upon spatial arrangements of both inorganic and organic constituents. Each MOF has been successfully synthesized.[26–28] The pore structure is colored in blue.

electrically conductive MOFs based on their connectivity. We then discuss the fundamental charging mechanisms of supercapacitors: electric double-layer capacitance and pseudocapacitance, and the techniques through which these may be studied. Focusing on 2D frameworks as the most studied materials class, we compare the performance of MOF electrodes with porous carbons, which highlights a number of challenges and opportunities for MOF research. Finally, we discuss new research directions that can push this emerging field forward.

2. Electroactive Metal–Organic Frameworks

MOFs are modular hybrid materials where the crystal structure, crystal morphology, and chemical structure can be varied over a wide space, giving rise to a diverse range of physical properties. While most MOFs are electrically insulating, it has recently been shown that appropriate choices of the organic and inorganic building blocks can be used to enable electrical conductivity and/or redox activity in the associated frameworks.[22–24] For example, passive Zr nodes can be replaced by redox-active building units containing transition metals with partial *d*-shell occupation, such as Co, Cu, or Ni. Alternatively, traditional carboxylate ligands can be substituted by a large variety of π-conjugated linkers that promote charge transport, such as triphenylamine or tetrathiafulvalene. MOFs can be classified based on the dimensionality of the connectivity between building blocks in their crystal structures: from 1D chains, to stacked 2D sheets and 3D networks (**Figure 1**). The dimensionality of MOFs is important because it impacts the accessible pore structure and internal surface area.[25]

Frameworks formed of low dimensional chains can be prepared by combining metals and bidentate organic linkers that favor one-directional growth (Figure 1).[25] The electrical conductivity of 1D MOFs, such as Ni(II) with 1,2,4,5-benzenetetramine ligand, and Cu(II) with 1,5-diamino-4,8-dihydroxy-9,10-anthraceneedione ligand, originates from the conjugated π-d system.[26,29] While an intrinsic pore structure is absent, mesopores can be formed from the voids between particles.[30] A large family of 2D MOFs has now also been established (Figure 1).[31] Electrically conductive 2D MOFs, such as $Ni_3(HITP)_2$, feature high in-plane π-d conjugation, resulting in high in-plane electrical conductivities.[19] They also exhibit electrical conductivity out-of-plane due to small interlayer distances as a result of π–π stacking between sheets.[22] The stacking structure generates unidirectional pore channels in the bulk material that are accessible to gases and liquids. In contrast, 3D MOFs have interconnected building units along three spatial dimensions, such as the prototype MOF-5 built from Zn_4O clusters bridged by 1,4-benzodicarboxylate with an interconnected pore structure. Some families of electrically conductive 3D MOFs have now also been reported,[32] and their exploration remains an active area of research.[28,33–36]

2.1. Microscopic Mechanisms of Capacitance

Energy storage in supercapacitors can be separated into two principal contributions: electric double-layer capacitance (EDLC) and pseudocapacitance (**Figure 2**).[1] EDLC is due to the electrostatic charge separation and the formation of an electric double-layer at the electrode–electrolyte interface (Figure 2a,b), while

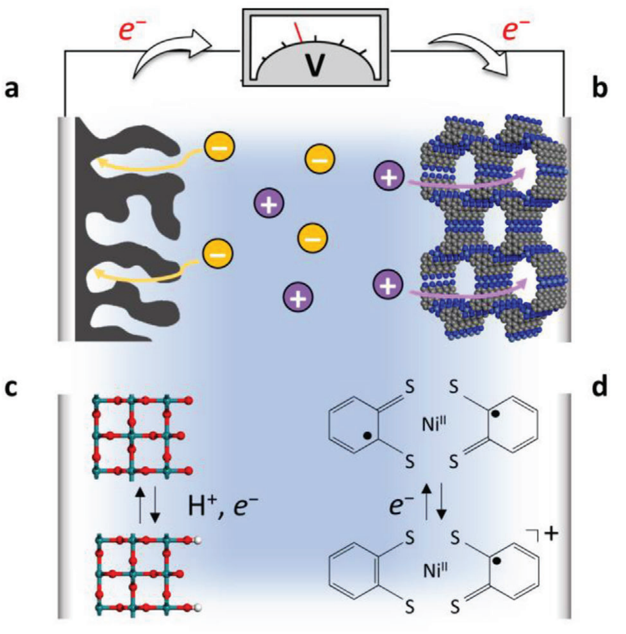

Figure 2. Different mechanisms of capacitive energy storage are illustrated for both traditional supercapacitor materials and electrically conductive MOFs. Double-layer capacitance develops at electrodes consisting of a) porous carbon and b) 2D MOFs with hexagonal pores.[21] Pseudocapacitive mechanisms with redox pseudocapacitance, as occurs in (c) RuO_2, and (d) MOFs with redox-active moieties.[37]

pseudocapacitance involves rapid reversible Faradaic reactions occurring at the electrode surface (Figure 2c,d).

EDLC primarily arises from charge separation occurring at the electrode–electrolyte interface, where ions in the electrolyte are adsorbed onto the electrode surface, forming an electric double-layer. This electrostatic charge separation leads to electric double-layer capacitance, which is typically associated with moderate capacitance values (of order 100 F g^{-1}) and fast charge/discharge rates (seconds to a few minutes). The electrode charge is in the form of delocalized electrons or holes as found for porous carbon electrodes and it is compensated by the electrolyte ions via counterion insertion, co-ion removal or ion-exchange mechanisms.[38,39] While EDLC has also been reported for MOF electrodes, these materials have a more inhomogeneous charge density distribution with more complicated polarization phenomena.[40]

On the other hand, pseudocapacitance involves rapid reversible redox reactions of electroactive species at the electrode surface, which can store additional charge beyond the EDLC. Pseudocapacitance is associated with Faradaic processes and typically results in higher capacitances (much larger than 100 F g^{-1}) than pure EDLC charge storage, but slower charge/discharge rates due to the involvement of redox reactions.[41] This mechanism is active in metal oxides, such as NiO, MnO_2, and RuO_2, where the electrode charge is in the form of localized small polarons. Interestingly, similar building blocks can be incorporated in MOFs, and it has been reported that MOF-based supercapacitors can exhibit pseudocapacitance.[37,42]

Assigning the active charging mechanism(s) in supercapacitors can require a combination of techniques. Initial experimental evidence for pseudocapacitance can include redox peaks in cyclic voltammetry curves, nonlinearities in Galvanostatic charge/discharge measurements, and low-frequency signatures in electrochemical impedance spectra. In materials modeling, the pseudocapacitive contribution can be realized by direct first-principles simulations, e.g., density functional theory (DFT), whether there exist oxidation state changes in the electrode or charge transfer between the electrode and electrolytes.

2.2. Studies of Charging Mechanisms

A range of in situ experimental techniques have been developed to characterize the charge storage mechanisms in supercapacitors. Nuclear magnetic resonance (NMR) spectroscopy, infra-red (IR) and Raman spectroscopies, small angle X-ray and neutron scattering (SAXS and SANS, respectively), and electrochemical quartz crystal microbalance (EQCM) techniques have all been used to investigate porous carbon EDLCs.[43] Due to the limitations of each technique in terms of the probed time- and length-scales, as well as differing chemical selectivities, these techniques are best employed in combination. For example, NMR spectroscopy can provide specific and quantitative information on the cations, anions, and solvent in supercapacitor electrolytes.[44] In contrast, decoupling and quantifying contributions from different electrolyte components is more difficult in EQCM, SAXS, and SANS, and is generally not possible with IR spectroscopy. However, NMR spectroscopy requires good NMR-active nuclei for study, and unambiguous quantification of charge storage mechanisms relies on good resolution of the resonances arising from in-pore species (in the electric double-layer) and free electrolyte species in the NMR spectrum.[45]

Both the thermodynamic and kinetic charging regimes can be probed with in situ experimental techniques. NMR spectroscopy has mainly been used to study thermodynamic charging mechanisms (i.e., under constant voltage equilibrium conditions) due to the relatively long times needed to obtain a single NMR spectrum and the slow charging times of the custom cells used for in situ measurements.[46] In contrast, EQCM measurements are generally made continuously as the cell state-of-charge is varied, and these measurements have been used to provide insights on the kinetic regime during charging.[43,47] In situ X-ray transmission measurements have also been used to study the kinetic charging regime, with different charging mechanisms observed depending on the charging rate.[48]

While the charging mechanisms of carbon-based EDLCs have been extensively probed, experimental work on MOF-based supercapacitorss is much more limited. Most prominently, He et al. employed in situ SANS to study the charging mechanism dynamics of $Ni_3(HITP)_2$ with sodium triflate in dimethylformamide (DMF) electrolyte.[49] It must be noted that the electrochemical performance of this system was not measured as part of this work. From fitting the changes in scattering intensity, they concluded that the dominant mechanism was dependent on the electrode polarization, with a charging mechanism intermediate between exchange and counter-ion adsorption suggested. The study reported that the MOF pores were ionophobic with this organic electrolyte (i.e., the ions are preferentially located outside the MOF pores). This was the first reported example of ionophobicity in MOF-based supercapacitors, and was interestingly in contrast to a computational study on the same MOF with an ionic liquid electrolyte, where the pores were found to be ionophillic.[50] Theoretical studies of model slit pores suggest ionophobic pores give rise to improved power and energy performances.[51,52] Given that this unusual ionophobic example has been identified in one of the first mechanistic studies of MOFs, this motivates further investigation of MOF-based supercapacitors to understand how ionophobicity is achieved, and its influence on supercapacitor performance.

EQCM has not yet been employed with MOF-based supercapacitors displaying primarily double-layer charge storage, but has provided insight into the charging of MOF-hybrid capacitors, alongside X-ray photoelectron spectroscopy (XPS) measurements.[53] Similarly, in the pseudocapacitor field, Cheng et al. investigated the charging mechanism of a series of catecholate MOFs using a combination of operando EQCM, and ex situ IR spectroscopy and XPS.[54] Faradaic charge storage mechanisms of MOF electrodes have also been studied using electron paramagnetic resonance (EPR), but only in Li-ion batteries.[55]

NMR spectroscopy has recently been used to probe molecular adsorption in MOFs, and Klug et al. highlighted that even in paramagnetic MOFs, high resolution NMR spectra may be obtained for guest species.[56] They demonstrated the potential of relaxation measurements and spinning sideband analysis to identify guest species in MOF pores for electrochemical applications.[56,57] However, there are no published mechanistic NMR studies of MOF-based supercapacitor charging to date. Similarly, IR spectroscopy and EPR have not yet been employed in the study of MOF charging, but have been applied in the identification of adsorbed guest species in MOFs and therefore show promise for studying MOF supercapacitors.[53,58–60]

In situ Raman spectroscopy was used by Lukatskaya et al. to explore the charge transfer mechanism in pseudocapacitive $Ni_3(hexaaminobenzene)_2$ ($Ni_3(HAB)_2$).[61] These experiments were accompanied by in situ X-Ray Absorption Near Edge Structure (XANES) measurements. Ex situ XANES measurements have also provided insight into the possible degradation pathways of some MOF-based supercapacitors by study of the metal oxidation states.[21,62] The application of XANES to MOF-based energy storage devices shows that techniques which have not typically been used to explore carbon EDLCs can be powerful in this new context.[63] The resulting range of unexploited experimental techniques available to understand charge storage and transfer processes in MOF supercapacitors presents exciting opportunities for future research.

Computational chemistry has also been employed to investigate charging mechanisms in supercapacitors. Molecular dynamics (MD) simulations have enabled the investigation of EDLCs during charging, especially for systems with porous carbon electrodes.[64,65] These studies have elucidated the charging mechanisms of EDLCs for both carbon nanotube electrodes with idealized model architectures,[66] and realistic porous carbon electrodes, which are challenging to construct.[67–69] The electrochemical environment was modeled based on the constant potential method, which applies an electric field in the simulation cell and describes the polarization of the electrode charges as a point charge distribution.[70]

Similar MD simulations have been employed to study the charging mechanism of MOFs with ionic liquids, focusing on the EDLC response.[50] This study elucidated the electrochemical interface of 2D MOFs and included both EDL structures and diffusion models, therefore giving information on both thermodynamic and kinetic phenomena. However, simple classical force fields cannot accurately describe polarization phenomena of the electrodes due to the absence of a realistic charge density distribution. In contrast to porous carbon electrodes, this becomes important for MOFs because of their heterogeneous electronic structures which arise from the distinct chemical building blocks.[64] An alternative theoretical approach is to describe the electrode charge density at a quantum mechanical level. Recently, the electrochemical interface of the MOF Cu_3HHTP_2 (HHTP = 2,3,6,7,10,11-hexahydroxytriphenylene) was studied with a multiscale quantum-mechanics/molecular-mechanics (QM/MM) methodology,[40] based on recent methodological developments on other electrochemical systems.[71–75] The polarization phenomena of the electrode were more accurately revealed by describing the MOF at the QM level. For the studied range of charge densities, it was found that the electronic charges (or holes) are localized solely on the organic ligand, and not the metal ion nodes. A counter-ion insertion mechanism for negatively polarized electrodes and a co-ion removal mechanism for positively polarized electrodes were shown to produce higher capacitances, respectively. Thus, these studies have begun to answer an open question in the field: "How does the charging mechanism affect the performance of a supercapacitor?".[43]

Using a quantum-mechanical description to study the charging mechanism of MOF-based supercapacitors becomes even more important when considering pseudocapacitance. DFT has been applied to explain the origin of high capacitance in some MOFs, which was found to arise from pseudocapacitance.[37,54] Collaborating with experimental measurements, phthalocyanine-based nickel-bis(dithiolene) (NiS_4)-linked 2D MOFs were studied with DFT and the redox mechanism was unveiled, with a two-step reduction reaction occurring on the MOF ligand.[37] It has also been found that intercalation-type pseudocapacitance mechanisms are also possible in MOF-based energy storage devices by matching experimental IR measurements with DFT results.[54]

2.3. Current Challenges for 2D MOFs in Supercapacitors

Over the past decade, several 2D electrically conductive MOFs have displayed promising performances in supercapacitor devices with a range of different electrolytes, often displaying specific and areal capacitances on par or exceeding traditional porous carbon electrode materials. Their performance is summarized in **Table 1** below.

Despite these promising performances, it is important to remind the community that there are currently several limitations of current 2D MOF systems compared to porous carbons. These are often neglected in published research, but can be clearly seen by comparing the capacitive performances of a standard porous carbon material, YP-50F, and a benchmark 2D MOF, $Ni_3(HITP)_2$ (**Figure 3**).[21,62]

Table 1. Summary of the performances of 2D conductive MOFs in supercapacitor devices with a range of different electrolytes. This includes the primary charge storage mechanism of the device (EDLC, pseudocapacitive, or unclear), the operating voltage or potential window, and a measure of the energy storage performance (F g^{-1} or mAh g^{-1}).

MOF electrode material	Electrolyte	Measurement type	Primary charge storage mechanism	Operating window	Energy storage performance	Refs.
$Ni_3(HITP)_2$	1 M NEt_4BF_4 in acetonitrile	Two-electrode	EDLC	0–1 V	111 F g^{-1} (0.05 A g^{-1})	[50]
$Ni_3(HITP)_2$	[EMIM][BF_4] ionic liquid	Two-electrode	EDLC	0–1 V	84 F g^{-1} (5 mV s^{-1}; best batch)	[50]
$Ni_3(HITP)_2$	0.5 M Na_2SO_4 in water	Two-electrode	EDLC	0–1 V	170 F g^{-1} (0.1 mA cm^{-2})	[76]
$Ni_3(HITP)_2$	1 M KOH in water	Three-electrode	EDLC	−0.1 to −0.6 V (vs Ag/AgCl)	100.8 F g^{-1} (1 mV s^{-1}; best morphology)	[77]
$Cu_3(HHTP)_2$	1 M NEt_4BF_4 in acetonitrile	Two-electrode	EDLC	0–1 V	129 F g^{-1} (0.05 A g^{-1}; best morphology)	[78]
$Cu_3(HHTP)_2$	[EMIM][BF_4] ionic liquid	Two-electrode	EDLC	0–1 V	57 F g^{-1} (0.05 A g^{-1}; best morphology)	[78]
$Cu_3(HHTP)_2$ (nanowire arrays)	1 M KCl in water	Two-electrode	Unclear	00.8 V	240 F g^{-1} (0.25 A g^{-1})	[79]
$Co_3(HITP)_2$ (exfoliated)	1 M LiTFSI in acetonitrile	Two-electrode	Pseudocapacitive	0–2.25 V	103 mAh g^{-1} (0.5 A g^{-1})	[80]
$Mn_3(HITP)_2$ (exfoliated)	1 M LiTFSI in acetonitrile	Two-electrode	Pseudocapacitive	0–2.25 V	89 mAh g^{-1} (0.5 A g^{-1})	[80]
$Ni_3(HAB)_2$	1 M KOH in water	Three-electrode	Pseudocapacitive	−0.75 to −0.25 V (vs Ag/AgCl)	427 F g^{-1} (0.2 mV s^{-1})	[81]
$Ni_3(HAB)_2$	0.5 M Na_2SO_4 in water	Two-electrode	Unclear	0–1 V	279 F g^{-1} (0.1 mA cm^{-2})	[82]
$Cu_3(HAB)_2$	1 M KOH in water	Three-electrode	Pseudocapacitive	−0.55 to −0.1 V (vs Ag/AgCl)	215 F g^{-1} (0.2 mV s^{-1})	[81]
$Cu_3(THQ)_2$	1 M KOH in water	Three-electrode	Pseudocapacitive	−0.3 to −0.9 (vs Ag/AgCl)	32 F g^{-1} (10 mV s^{-1})	[83]
$Cu_3(THQ)_2$-BPY (pillared)	1 M KOH in water	Three-electrode	Pseudocapacitive	−0.3 to −0.9 V (vs Ag/AgCl)	66.1 F g^{-1} (10 mV s^{-1})	[83]
$Ni_3(BHT)_2$	1 M $LiPF_6$ in acetonitrile	Three-electrode	Unclear	0 to −1.7 V (vs OCP; Ag pseudoreference)	245 F g^{-1} (3 mV s^{-1})	[84]
$Ni_3(BHT)_2$	1 M NEt_4PF_6 in acetonitrile	Three-electrode	Unclear	0 to −1.7 V (vs OCP; Ag pseudoreference)	36 F g^{-1} (5 mV s^{-1})	[84]
$Ni_3(BHT)_2$	1 M NEt_4BF_4 in acetonitrile	Three-electrode	Unclear	0 to −1.7 V (vs OCP; Ag pseudoreference)	29 F g^{-1} (5 mV s^{-1})	[84]
$Ni_3(BHT)_2$	1 M NBu_4BF_4 in acetonitrile	Three-electrode	Unclear	0 to −1.7 V (vs OCP; Ag pseudoreference)	31 F g^{-1} (5 mV s^{-1})	[84]

Both systems were assembled as symmetric cells with a standard organic electrolyte, 1 M NEt_4BF_4 in acetonitrile. While $Ni_3(HITP)_2$ displays both specific and areal capacitances exceeding YP-50F porous carbon when charged at a low current density of 0.05 A g^{-1} (111 F g^{-1} and 18 μF cm^{-2} compared to 100 F g^{-1} and 6 μF cm^{-2} for YP-50F across their respective double-layer voltage windows), $Ni_3(HITP)_2$ displays a number of limitations which reduce its overall performance in supercapacitors:

1) **Limited stable voltage window**. $Ni_3(HITP)_2$ has a significantly smaller stable voltage window of ˜1–1.5 V, compared to ˜2.5–2.7 V for YP-50F porous carbon (Figure 3c and Table 1).[67,85–91] As a result, despite the comparable specific capacitance of $Ni_3(HITP)_2$, it has both a lower energy and power density compared to YP-50F porous carbon, as both quantities are dependent on the square of the operating voltage window. This drawback is also seen in many other 2D MOFs, with all MOFs that have been studied with organic electrolytes in the literature having lower stable voltage windows than porous carbons (Table 1).[18,62,80,84] This often-ignored disadvantage is a major challenge for the field, and more research is needed to understand and improve the operating voltage windows of 2D MOFs, which would increase both their energy and power densities. One promising route may be to vary and optimize both the metal and ligand present in the MOF. Comparing the stability of $Ni_3(HITP)_2$ and $Cu_3(HHTP)_2$ reported in the literature reveals that changing the metal-ligating group combination can modify the stable voltage window.[21,62] Further optimization of the metal–ligand combination could find more electrochemically stable combinations with wider stable voltage windows, potentially allowing for MOFs to compete with porous carbons in terms of energy and power densities in the future. We believe that developing a better understanding of the degradation mechanisms of current MOF-based

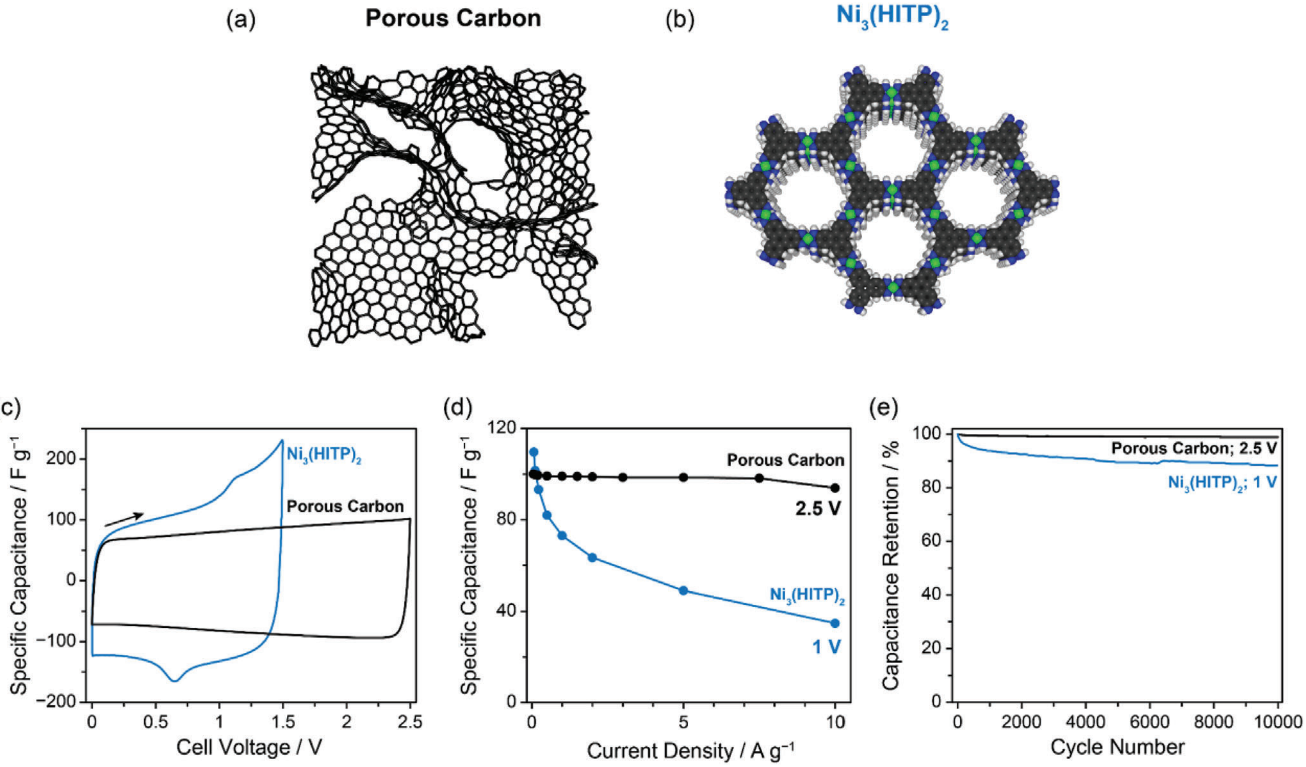

Figure 3. Comparison of the performances of a) YP-50F porous carbon, and b) $Ni_3(HITP)_2$ in symmetric supercapacitor cells with 1 M NEt_4BF_4 in acetonitrile electrolyte, as reported in the literature.[21,62] This shows the differences in (c) stable voltage window and capacitance, d) rate/power performance, and e) cycling stability at 2 A g^{-1} between porous carbons and current 2D MOF electrode materials. Note that, although an overall stable voltage window of approximately 1.5 V was found for $Ni_3(HITP)_2$, charging and cycling experiments in (d) and (e), respectively, were performed in the double-layer stable region of 0–1 V.

supercapacitors that occur at higher voltages is crucial to tackling this challenge.

2) **Poor rate performance**. Another disadvantage of current MOF systems is their lower rate/kinetic performance compared to carbon electrode materials. In the above work, $Ni_3(HITP)_2$ exhibits a drop in capacitance to ~32% of the initial value as the current density is increased from 0.05 to 10 A g^{-1} with charging across its stable double-layer voltage window of 0–1 V. This rate capability is significantly lower than that for YP-50F porous carbon (94%) in the same current density range (Figure 3d). Once again, this behavior is seen in other 2D MOFs studied in the literature, with all current examples showing significantly reduced rate performances compared to traditional carbon materials.[18,62,85,80,84] As a result, lower current densities, and therefore longer charging and discharging times, are needed to achieve high capacitances with 2D MOFs, which is undesirable for practical applications. The lower kinetic performance of 2D MOFs may be due to several factors, including lower electrical conductivities. Slower diffusion of electrolyte ions within 2D MOFs also impacts rate performances, and this needs to be improved in the future. Recent studies employing $Cu_3(HHTP)_2$-based electrodes, first in supercapacitors and then in Li-ion batteries, have shown that changing the morphology of 2D MOFs is a promising route to tune charging kinetics and rate performances.[78,92] In both works, it was found that "flake" particles, with extended growth in the ab plane and a pore network of many short pores, displayed better rate performances than "rod" particles, with extended growth in the c plane and longer pores. This was due to improved ion kinetics in the "flake" particles, with shorter pores being more rapidly accessible to electrolyte ions. We hypothesize that further tuning of the morphology would yield further improvements in rate performance.
3) **Lower cycling stability**. The final challenge facing current 2D MOFs is their lower cycling stability. Dincă et al. reported the cycling stability of $Ni_3(HITP)_2$ as ~90% when cycled for 10 000 cycles between 0 and 1 V at 2 A g^{-1}. While this is encouraging, it is lower than the cycling stability for YP-50F porous carbon under similar conditions, which had a capacitance retention of almost 99% despite the larger maximum cell voltage used (Figure 3e). Once more, this is not unique to $Ni_3(HITP)_2$, with $Cu_3(HHTP)_2$ also exhibiting a decreased cycling stability compared to YP-50F porous carbon.[62] This further limits the real-life applications of current MOF-based supercapacitors. As noted previously, more work is needed to understand the mechanisms that cause these frameworks to degrade during electrochemical cycling. This would guide the design of new 2D MOFs with improved electrochemical stabilities.

In summary, current state-of-the-art 2D MOFs suffer from several limitations that reduce their overall performance in supercapacitors compared to porous carbons. These challenges must be overcome if 2D MOFs are going to become competitive in practical devices in the future.

3. Opportunities

Despite the current challenges facing MOF-based supercapacitors, the crystalline and highly tuneable structures of MOFs open the door to exciting new studies that are difficult to perform with traditional carbon electrode materials to assess how electrode structure impacts supercapacitor performance. At the same time, they will enable new mechanistic studies so that the charging mechanisms leading to improved performance can be understood. We envisage that MOF chemistry can be tuned to both gain insights into ideal electrode properties and improve their overall supercapacitor performance in the following ways.

1) **Modification of pore size**. By changing the size of the aromatic core of the linker molecule, 2D MOFs can be synthesized with a range of different well-defined pore sizes. MOFs made using benzene-, triphenylene-, and trinaphthylene-based linkers have all been reported in the literature, and those made from both benzene- and triphenylene-based linkers have been shown to perform well in supercapacitors (Table 1).[21,81,27,93–95] Changing the pore size represents a promising way to improve the capacitances of MOF supercapacitors, and new MOFs and ligands are being synthesized to allow for greater variation in pore sizes.[96–98] Furthermore, systematic structure–performance studies can be performed using these frameworks to gain insights into the optimal pore size for supercapacitors.
2) **Modulation of framework dimensionality**. The dimensionality of MOFs can be modulated post-synthetically via pillar-ligand insertion. This leads to a change in dimensionality from 2D to 3D, resulting in changes to both the electronic structure and the pore structure. Initial work on modifying the dimensionality of CuTHQ (THQ = tetrahydroxyquinone) by Park et al. has suggested that pillaring can increase ion accessibility into the pores, resulting in an increased specific capacitance compared to their 2D counterparts (Table 1).[83] More work needs to be done with a wider range of 2D MOFs, as well as inherently 3D MOFs, to study the impact of structural augmentation in greater detail. Pillaring of 2D MOFs may also help to improve ion mobility within the frameworks.
3) **Inclusion of well-defined functional groups**. The well-defined structures of 2D MOFs allow for the systematic inclusion of specific functional groups that is challenging in porous carbons, where a distribution of functional groups is normally present. Many such functionalized linkers have been synthesized in recent years, and employing these materials as supercapacitor electrodes may unveil detailed structure–performance relationships to correlate specific functional groups with supercapacitor performance, leading to general design principles for carbon-based supercapacitors.[96,97,99] Furthermore, inclusion of specific functional groups will change electrolyte-MOF interactions in devices, modifying the double-layer structure and potentially yielding further improvements to the performances of MOF-based devices. Modifying MOF-electrolyte interactions in existing systems by changing the electrolyte is also a promising avenue for exploration, as shown by recent work from Dincă et al., who demonstrated that Li-ion electrolytes result in significant increases in the specific capacitance of nonporous $Ni_3(BHT)_2$-based (BHT = benzenehexathiolate) supercapacitors (Table 1).[84] The impact of the electrolyte on the performance of MOF-based supercapacitors has been further highlighted in work from Forse et al., who showed that $Cu_3(HHTP)_2$ displays dramatically lower capacitances and rate capabilities with an ionic liquid electrolyte (EMIM-BF_4) compared to an organic electrolyte (1 M NEt_4BF_4 in acetonitrile).[78] This drop in performance was more significant than that seen for porous carbons with the same electrolytes.[100] This is further evidence for the poor movement of ions through the ordered pores of 2D MOFs, and is supported by results with $Ni_3(HITP)_2$.[50] This shows that it is important to use electrolytes with high ionic conductivities in 2D MOF-based supercapacitors.
4) **Pseudocapacitive contributions**. Both modification of the functional groups in MOF linkers and tuning MOF-electrolyte interactions could lead to pseudocapacitive contributions to charge storage. MOFs have two possible redox-active sites, the metal node(s) and the organic linker with multiple ion adsorption sites. These can be exploited to enhance capacitive performances through rapid redox reactions, as shown in work with HAB (hexaaminobenzene) MOFs (Table 1).[81,61] Such pseudocapacitive contributions are currently underutilized in MOF-based energy storage devices, and more work needs to be done to exploit the potential of pseudocapacitive MOF electrodes.

In parallel, mechanistic studies should be carried out to determine charge storage mechanisms and to uncover further design principles for improved MOF supercapacitors. There are a number of open questions including; where are the electrons and holes localized in the electrode structure? How are the charges on the solid electrode compensated by the charges from the liquid electrolyte? What are the chemical environments of the charge compensating ions? How does the chemical structure of the MOF impact the charging mechanisms? Which processes drive degradation during prolonged cycling?

1) **Experimental studies of the charging mechanisms**. Complementary experimental techniques should be used in an attempt to answer the questions surrounding charge storage and transfer in MOF supercapacitors. So far, only one study has utilized multiple techniques in an attempt to do so.[61] This slow progress evidences the significant experimental challenges surrounding MOFs compared to the study of carbon-based EDLCs. First, the low air-stability of many conductive MOFs may make in situ experiments more complex to set-up. Furthermore, their often low electrochemical stability windows could make elucidation of the charging mechanisms difficult due to limitations in sensitivity of experimental measurements. To expand the limits of the stable potential window, the degradation mechanisms should be explored and understood through XANES and EPR studies which can probe both the metal and the linker environments.[63] For determination of the chemical environments of the charge compensating ions, NMR spectroscopy

is a useful technique as it is sensitive to the local environments of the cations and anions. Furthermore, the applications of NMR spectroscopy in the field may be extended to provide insight on the impact charging has on the MOF structure, including in pseudocapacitive mechanisms and degradation.[101] However, this technique is similarly subject to challenges. As noted previously, NMR studies of charging mechanisms rely on good resolution of the chemical environments (which is generally the case for porous carbons due to ring-current shifts,[102] but will likely be less predictable in MOFs), and second many electrically conductive MOFs are inherently paramagnetic, causing significant broadening in the NMR spectra and hence exacerbating the problem of resolution.

Once breakthrough studies have been made to establish standard experimental techniques for studying the charging mechanisms of MOFs, they may then be routinely employed to determine how the chemical structure of the MOF impacts the charging mechanisms. However, while the structures of MOFs are more tuneable than porous carbons, the compounds must be well-characterized to probe the influence of defects, and changing the MOF structure is likely to have impacts on its suitability for a given technique. For example, in NMR spectroscopy, a change in functional group could change the spectral resolution of chemical environments significantly, while a change in the oxidation state may lead to a paramagnetic MOF which will be more challenging to study with NMR. This emphasizes the need for a plurality of experimental techniques, especially those which have not been widely used in earlier studies of carbon EDLCs, such as EPR and XANES.

2) **Computational studies of the charging mechanisms**. While porous carbons have complex amorphous structures which are challenging to model, the crystalline structure of MOFs enables molecular simulations that can much more accurately represent the experimental systems. MD simulations are an effective tool to study a variety of properties of MOF supercapacitors, including ion transport and electrochemical performance. It is crucial to describe the electrode–electrolyte interface from first-principles, e.g. with DFT, to describe any electron transfer processes, a key factor in pseudocapacitance, as well as to describe the heterogeneous electron density on the electrode from EDLC contributions. However, it is not currently possible to describe all components of a supercapacitor from first-principles for MD simulation. The recently developed QM/MM method is ideal for investigating MOF-based systems,[40] and machine learning force fields may also contribute to investigating the interface in the future based on their recent rapid development.[103,104] Those methods may not only help to understand the in-pore electric double-layer structure but can also describe chemical reactions at the interface. However, it is still challenging to find a proper method that can capture both the kinetic and thermodynamic phenomena at the same time due to the high computational cost. Therefore, employing classical MD simulation is still important to understand the kinetics of MOF supercapacitors, and advanced charge equilibration methods are needed.

In conclusion, in this perspective we have discussed the emerging field of MOF supercapacitors. MOFs have shown promise as supercapacitor electrodes, both through EDLC and pseudocapacitive contributions to energy storage, and their capacitances can exceed those of traditional electrode materials. However, our comparison of the performance of a state-of-the-art MOF with a typical porous carbon electrode highlights several challenges. The MOF electrodes suffer from lower stable potential windows, shorter cycle lifetimes, and slower charging rates than porous carbons, raising questions about their practical applicability. Excitingly, the highly tuneable structures of MOFs offer several potential solutions to these issues, some of which have already been realized. For example, the charging rates of 2D frameworks have been improved through morphology control, and optimization of the framework dimensionality, surface chemistry, and pore size may lead to further improvements in the future. Improving the stability of these materials poses a greater challenge, with the path forward more unclear. The optimization of MOF electrodes will ultimately be guided by a fundamental understanding of the charging and degradation processes. The electronic and ionic structure changes that occur during charging are only just beginning to be elucidated, while degradation mechanisms have barely been explored. The development of in situ experimental methods as well as molecular simulations is required to understand the fundamentals of energy storage in MOFs so that improved materials may be designed and synthesized in the future. Ultimately, we also expect that some of the challenges and opportunities discussed in this perspective will also apply to other framework electrode materials, such as covalent-organic frameworks.[105,106]

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Conflict of Interest

The authors declare no conflict of interest.

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