

REVIEW ARTICLE

<https://doi.org/10.1038/s42004-019-0184-6>

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Metal-organic framework functionalization and design strategies for advanced electrochemical energy storage devices

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Metal-organic frameworks (MOFs) are a class of porous materials with unprecedented chemical and structural tunability. Their synthetic versatility, long-range order, and rich host-guest chemistry make MOFs ideal platforms for identifying design features for advanced functional materials. This review addresses synthetic approaches to control MOF attributes for realizing material properties such as charge conductivity, stability, surface area, and flexibility. Along with an updated account on MOFs employed in batteries and supercapacitors, new directions are outlined for advancing MOF research in emergent technologies such as solid-state electrolytes and battery operation in extreme environments.

Global demands for clean energy storage and delivery continue to push developing technology to its limits. Batteries and supercapacitors are among the most promising technologies for electrical energy storage owing to their portability and compact size for on-demand usage. Despite their promise, chemical and physical limitations of existing materials hinder performance and require new, creative solutions. For instance, polymers and conductive carbon materials are relatively inexpensive, scalable, and synthetically tunable but can lack physical and chemical stability for device implementation. On the other hand, solid inorganic materials, such as metal oxides and silicon, are used as electrode materials due to their robust structure and redox-active sites. However, sluggish ion diffusion of metal oxides limit charge/discharge rate capabilities and large volumetric changes lead to mechanical instability. Drawbacks in these current platforms motivate the discovery and development of new materials for advanced energy storage devices.

Metal-organic frameworks (MOFs) are attractive candidates to meet the needs of next-generation energy storage technologies. MOFs are a class of porous materials composed of metal nodes and organic linkers. Their modular nature allows for great synthetic tunability, affording both fine chemical and structural control. With creative synthetic design, properties such as porosity, stability, particle morphology, and conductivity can be tailored for specific applications. As the needs of each energy storage device are different, this synthetic versatility of MOFs provides a method to optimize materials properties to combat inherent electrochemical

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limitations. Porosity, a defining characteristic of MOFs, is also highly important for guest/ion storage and transport. Moreover, the plethora of multidisciplinary characterization techniques applicable to MOFs allows a multitude of experiments to illuminate underlying determinants of performance and provide key insight for development of next-generation materials. The facile tunability of MOFs also enables their utilization as precursors and templates in creating functional materials with desired chemical composition and unique morphologies. MOF-derived materials, including metallic compounds, porous carbons, and their nanocomposites are being widely investigated¹. Tuning MOF precursor composition and manipulating conversion processes are two main strategies for chemical and structural control. MOF derivatives have shown great potential in electrocatalysis and energy storage devices^{2,3}.

Herein, we will discuss how unique design strategies of MOFs can be employed to impart select materials functionalities for advancing both performance and fundamental understanding in energy storage devices (Fig. 1). As there are a number of recent reviews on the progress of MOFs for batteries and supercapacitors^{4–9}, we instead focus on select MOF attributes that can serve as tunable parameters for modifying porous materials. We will then identify current pitfalls and knowledge gaps of different energy storage technologies and how MOF design strategies can overcome these challenges. We will end our review with the emerging technologies that will particularly benefit from these MOF attributes, providing an instructive roadmap for future MOF research in advanced energy storage devices.

Tunable MOF attributes for electrochemical applications

In this section, we will discuss synthetic strategies to tune MOF properties for specific needs in electrochemical applications (Fig. 1). We focus our attention on (i) physical and chemical properties, (ii) porosity and high-surface area, (iii) charge conduction, and (iv) scalability and processability.

Physical and chemical properties. MOFs are renowned for their ability to impart functionality using judicious selection of linkers and metal nodes. Several comprehensive reviews have already highlighted the multitude of synthetic strategies to tune the chemistry, stability, particle size, and flexibility of the

framework^{10–12}. MOFs can also undergo “post-synthetic modification” to further tune properties through swapping, altering, or altogether removing linker or node components in the framework. In addition, select crystallographic phases and crystallite size/morphology can be controlled to modify the surface chemistry of the MOF¹³. The ability to tune such properties is a defining strength of this unique class of porous materials as it provides strategic control over host–guest chemistry for energy storage applications.

Importantly, the electrochemical stability of MOFs can be enhanced by selection of appropriate synthetic parameters. For instance, MOFs composed of redox-inactive nodes and shorter, more rigid linkers exhibit greater thermal and chemical stability. On the other hand, high porosity and flexibility allow superior ion storage and transport. Mechanical properties can be tuned by introduction of flexible linkers, modulation of host–guest interaction strength, construction of multi-metallic frameworks, and manipulation of crystal size^{14,15}. Structural rigidity may prove necessary for electrodes that experience dendrite formation, which can lead to dangerous short-circuiting. Conversely, MOF malleability would be particularly useful to maintain structural integrity in devices where the active material undergoes volume expansion and contraction. In addition, stimuli-responsive flexible MOFs could be realized as a safety feature, where temperature, voltage, or mechanical signal induces a “shut-off” mechanism to protect both the device and the user.

Porosity and high-surface area. MOFs are perhaps most famous for their extraordinary porosity and surface area. The pore size and topology of the framework can be finely tuned by selecting appropriate linkers and metal nodes. Isorecticular MOFs, defined as frameworks with the same structural topology, are formed by using a library of related organic linkers with different lengths and functionalities^{16–18}. The tremendous control over pore size and chemical environment in isorecticular MOFs provides the ability to independently observe structural and chemical factors that impact electrochemical processes. Hierarchically porous MOFs—frameworks containing a combination of micropores and mesopores—further create strategic channels and pore space that can influence molecular diffusion. Higher surface area is also favorable for catalytic processes, such as oxygen reduction (ORR)

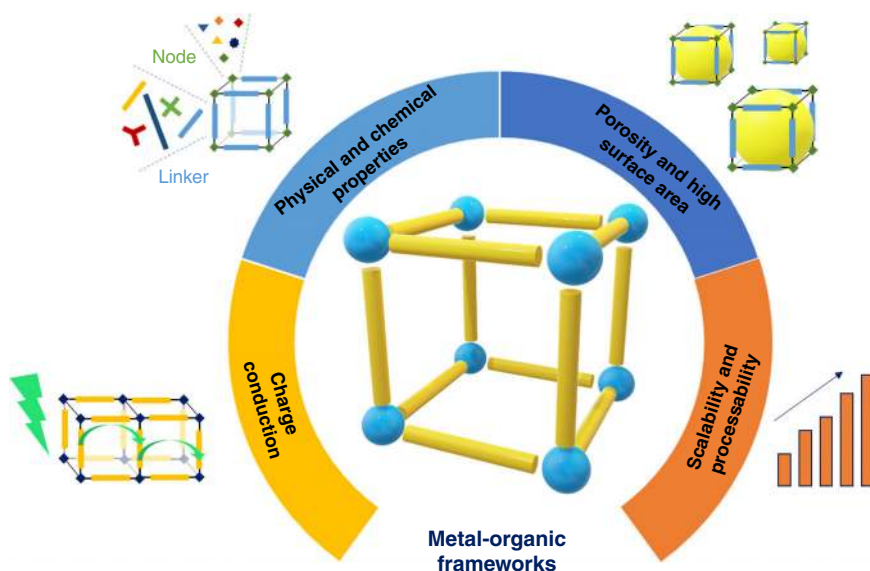


Fig. 1 Tunable MOF attributes for electrochemical applications. MOFs can be scaled, processed, and functionalized to impart new physical and chemical properties, charge conduction, and adjustable porosity

in lithium-oxygen batteries. This capability to tune porosity and surface area is unprecedented in conventional inorganic solids and represents an opportunity for electrochemical applications.

Charge conduction. Both electronic and ionic transport are paramount in electrochemical devices. Large overpotentials caused by high internal resistances reduce device output power and limit the efficiency of batteries and supercapacitors. Emergent synthetic strategies for enhancing ionic and electronic conductivity in MOFs not only avail new materials for charge transport applications, but also provide novel molecular insights for materials discovery beyond porous organic frameworks.

While there has been an explosion of new MOFs in the last two decades, most frameworks are insulating due to the common use of metal-oxygen linkages. To overcome this challenge, significant research efforts are aimed at tailoring the electronic structure via both metal and linker contributions using an approach termed “through-bond” conductivity. For instance, utilizing the loosely bound *d*-electrons in Fe²⁺ and soft sulfur linkers led to an enhancement in electronic conductivity by six orders of magnitude compared to the analogous Mn-S bonds in M₂(dsbdc) MOFs and ten times improvement compared to metal-oxygen linkages in M₂(dobdc)¹⁹. Another approach for improving electron conduction involves “through-space” via π - π interactions or by electron hopping to guest molecules^{20,21}.

There are several strategies employed to modulate the ionic and protonic conductivity in MOFs. The simplest method is to incorporate ionic guest species that can facilitate transport. Polar functionalities can be integrated into the framework post-synthetically, allowing the potential for spatial and directional transport control^{22–24}. In addition, ionic frameworks with mobile counter ions substantially can boost the ionic conductivity^{25–27}. While proton conductivity in MOFs has been extensively studied due to recent interest in hydrogen fuel cells, ionically conductive MOFs are predicted to see tremendous research activity owing to the mounting demand for solid-electrolyte materials in energy storage devices.

The diverse strategies for tuning chemical, electronic, structural, and mechanical properties in MOFs are undoubtedly strengths for electrochemical applications. However, different energy storage devices have different priorities for materials properties. Understanding the needs of individual device components are critical for selecting the appropriate design elements and synthetic methods. For example, high MOF porosity permits the storage of active species, which is particularly beneficial for devices that rely on chemical conversion of small molecules (e.g., polysulfides and O₂ in lithium-sulfur and lithium-oxygen batteries, respectively). This requirement would place a preference for “through-bond” over “through-space” strategies to enhance electronic conductivity.

Scalability and processability. The dramatic popularity of MOFs in the last 20 years makes it difficult to remember that MOF research is still a nascent field. In order to move these novel materials from the laboratory to commercial applications, scalability and processability of MOFs are necessary areas of research. On the scalability front, MOF syntheses have been demonstrated in large-scale production by current companies (BASF, MOF-WORX, MOF Technologies, and NuMat)^{28–30}. These companies take advantage of flow chemistry, electrochemistry, and mechanochemistry methods. Mechanochemical MOF synthesis methods utilize physical mixing (grinding, ball-milling, etc.) of linker and node components without the need for solvents or prolonged heating, which reduces cost and chemical waste³¹. Mechanochemical syntheses are also amenable to creating mixed-

metal MOF bulks by altering the component reagents. The use of cheaper metal sources such as metal salts, oxides, hydroxides, or carbonates can further lower the cost of production. Another creative method for enhancing scalability of MOFs is microwave irradiation (MI), which can rapidly generate MOFs from precursor solutions^{31–33}. Microwave heating requires less energy than traditional solvothermal methods, as MI syntheses rely on localized heating rather than heating the entire solution.

As the formation of MOFs only requires a few simple chemical building blocks, MOFs are quite attractive for processing into electrochemical devices. Solution-phase layer-by-layer (LBL) deposition, which have led to a class of materials called SURMOFs, enable molecular and structural precision as well as film thickness control. Electrochemical synthesis methods promote rapid and uniform MOF growth and allow direct deposition onto conductive platforms with precise layer deposition thicknesses^{34–36}. Even finer control over film thickness is possible through vapor deposition, such as atomic layer deposition (ALD) and chemical vapor deposition (CVD), which has been used to grow MOFs on flat surfaces as well as fibers^{37–39}. The diversity of possible substrates and extensive layer control expand the possibilities for MOF electrochemical applications.

Targeting design strategies for energy storage devices

Utilizing the strategies discussed above, the following sections will highlight recent use of key design elements in MOFs to target specific challenges in various energy storage devices (Fig. 2a–d).

Metal-ion batteries. Metal-ion batteries are a class of rechargeable batteries that rely on ion insertion and extraction from the battery electrodes. In a typical charging cycle, metal ions from the cathode (positive electrode) and the electrolyte migrate and insert into the anode material (negative electrode), while energy is discharged in the reverse process (Fig. 3a). Lithium-ion batteries (LIBs) are widely employed as energy storage devices in consumer electronics and are currently the industry standard for electric vehicles. However, the limited energy density and high cost of LIBs have motivated exploration of novel electrode materials as well as the development of sodium-ion batteries (SIBs), both of which have larger theoretical capacities per ion and more abundant metal-ion precursors.

The largest challenges in current metal-ion anodes are their low specific capacity and limited rate performance. Specific capacity is defined by the total charge that can be stored in the device per mass of active material with typical units of mAh g⁻¹. The performance is also measured by rate capability (specific capacity as a function of charge and discharge rates) and capacity retention upon extended cycling (percentage of the maximum specific capacity as a function of cycle number). Most LIBs utilize a graphite anode which relies on the reversible intercalation of Li ions in the layered carbon material. However, graphite anodes has a specific capacity of ~350 mAh g⁻¹, which places an upper limit on the total energy density of metal-ion batteries⁴⁰. In addition, dendrite formation in LIBs can lead to thermal runaway and cell deformation, introducing significant engineering challenges for large-capacity storage and reliable long-term cycling. Silicon anodes are an attractive alternative with a specific capacity of 4200 mAh g⁻¹, but significant volume expansion poses serious safety concerns⁴¹. These technical hurdles in metal-ion anodes necessitate creative remedies and the exploration of new electrode materials.

With their versatile structures, redox-active functionalities, high porosity, and remarkable host-guest chemistry, MOFs can play key roles in metal-ion anodes. For example, redox-active metal centers and lithium-stabilizing ligand moieties can boost

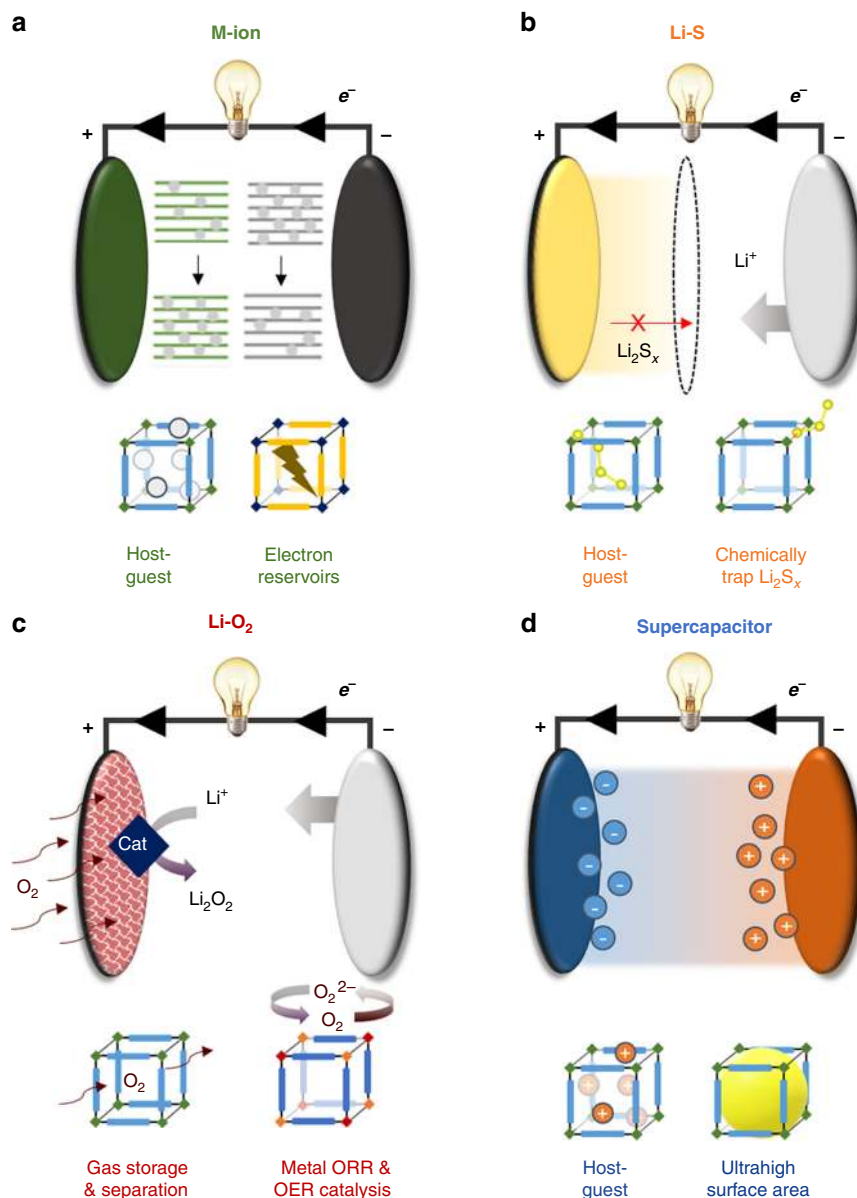


Fig. 2 Unique MOF properties for targeting specific challenges in energy storage devices. **a** Metal-ion batteries rely on host-guest interactions to store ions while installation of electron reservoirs can improve charge conduction and increase deliverable capacity. **b** Lithium-sulfur batteries use host-guest interactions to store lithium and sulfide ions. Functional groups can be also used to trap polysulfides and diminish capacity loss. **c** MOFs can serve as selective gas sieves and as gas storage media in lithium-oxygen batteries. The metal nodes can also serve as oxygen reduction (ORR) or evolution catalysts. **d** The high porosity and host-guest nature of MOFs can be used to store charged species in supercapacitors

the amount of stored Li ions, and therefore increase the theoretical capacity. The innate porosity of MOFs can allow for reversible storage of metal ions and provide significant interfacial contact with the electrolyte solution to facilitate ion transport.

Installation of electron reservoirs: The high synthetic tunability of MOFs is particularly advantageous for the installation of novel electron reservoirs for metal-ion battery electrodes. Redox-active metal nodes are fairly standard in MOF construction, and have been heavily explored in both cathode and anode materials as listed in previous reviews^{4–7}. Recent demonstrations of this design strategy is reported in novel polyoxometalate-based MOFs for LIB anodes^{42,43}. The redox-active polyoxometalates (POMs) enable significantly enhanced Li^+ insertion/extraction, while the stability of the POM unit further promotes long-term cycling capabilities (Fig. 3b). The cluster of metal ions in POMs can similarly be integrated in the MOF node structure, and represent

a viable method to increase the electron storage capacity of POM–MOF hybrids.

Redox-active linkers can also serve as electron reservoirs within the material framework. Most linkers already contain benzene, pyridine, imidazole, or thiophene subunits that can be electrochemically active. Quinone-based MOFs could also be utilized for energy storage applications via reduction of the quinone to the semi- and hydroquinone compounds. Addition of linkers with accessible reduction/oxidation potentials can extend the theoretical capacity beyond the capabilities of metal node without sacrificing porosity or framework integrity.

Utilizing electronically conductive MOFs: Incorporation of electronically conductive frameworks in metal-ion anodes can improve rate performance at high current densities. For example, a conductive cobalt-based MOF has been demonstrated as an effective anode material for SIBs⁴⁴. This 2D framework is composed

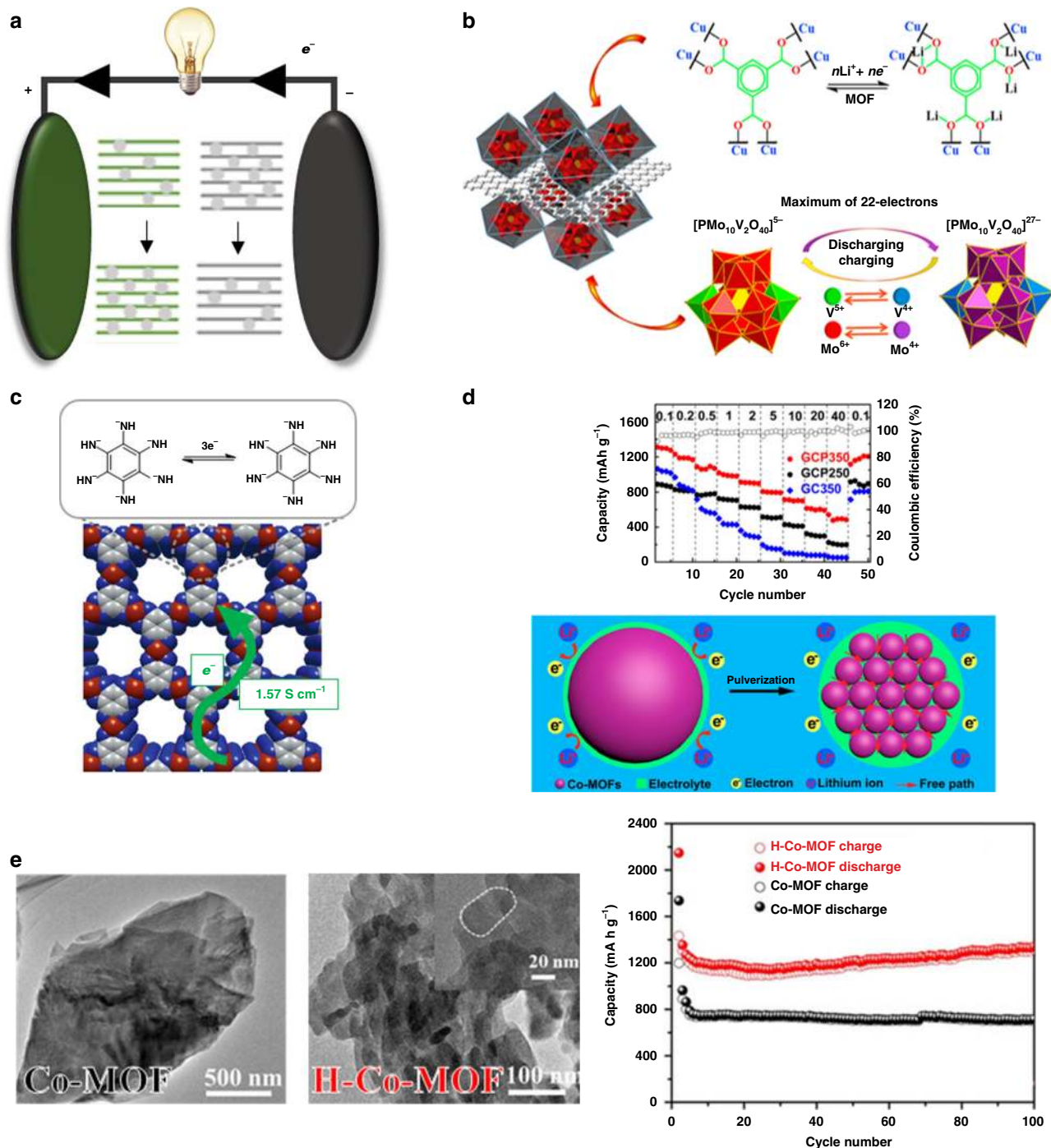


Fig. 3 Various strategies implementing MOFs for metal-ion batteries. **a** Metal-ion battery schematic. **b** Installation of electron reservoirs in the organic linkers and introduction of POM clusters (adapted with permission from ref. ⁴³ © 2017 Elsevier). **c** Use of Electronically conductive 2D Co-HAB MOF for SIBs (adapted with permission from ref. ⁴⁴ © 2018 American Chemical Society). **d** Reduced Co-MOF particle size improves rate capability and deliverable capacity (adapted with permission from ref. ⁵² © 2018 American Chemical Society). **e** Construction of a hierarchically porous H-Co-MOF similarly increases battery capacity (adapted with permission from ref. ⁵³ © 2018 John Wiley and Sons)

of hexaaminobenzene (HAB) linkers connected by Co(II) centers (Fig. 3c). Owing to the high degree of delocalization in this graphene-like network, Co-HAB has a reported electronic conductivity of 1.57 S cm^{-1} . Moreover, the redox-active nature of the Co centers and the aromatic system enable stable capacities of 200 mAh g^{-1} over 100 cycles at high rate of 4 A g^{-1} . Co-HAB also demonstrates remarkable performance at high rates (up to 12 A g^{-1}) and the ability to recover capacity when returned to more moderate cycling rates. Effective cycling at high charge/discharge

rates was also demonstrated by another moderately conductive MOF (Cu-CuPc, reported conductivity $1.6 \times 10^{-6} \text{ S cm}^{-1}$) that was able to achieve $\sim 150 \text{ mAh g}^{-1}$ at a rate of 5.2 A g^{-1} for LIB cycling⁴⁵. These examples demonstrate that with the appropriate design features, MOFs have the potential to withstand extraordinary cycling conditions.

Porosity for tuning ionic conductivity: The long-range order and porosity of MOFs can play a unique function in modulating ion transport. In SIBs, the large ionic radius of Na^+ leads to slow

diffusion compared to Li^+ , making it critical to have well-designed anode materials with available ion transport pathways^{46,47}. Of the MOFs studied for LIB anodes, most frameworks utilize relatively short linkers such as 1,4-benzenedicarboxylate acid (bdc), fumaric acid, and formic acid that yield MOFs with small pore sizes^{48–50}. To improve the sluggish diffusion of Na^+ , the common bdc linker was extended using 4,4'-biphenyldicarboxylic acid (bpdc) to form an isorecticular Co-based MOF⁵¹. The authors showed that the longer linker results in a MOF with larger pores that is better suited to facilitate Na^+ diffusion. In SIB devices, this MOF anode exhibited stable capacities of $\sim 200 \text{ mAh g}^{-1}$ over 1000 cycles at a charge rate of 100 mA g^{-1} . Isorecticular MOFs and structurally flexible frameworks thus presents a rare opportunity to correlate porosity and chemical functionality with metal-ion transport.

Increasing the external surface area of the MOF crystallites, either by manipulating particle size or shape, can also shorten the ionic diffusion length. Reducing the Co-based MOF the particle size from $\sim 100 \text{ nm}$ to $< 5 \text{ nm}$ led to stable capacity delivery of 1301 mAh g^{-1} at low rate of 0.1 A g^{-1} and superior rate performance of 494 mAh g^{-1} at 40 A g^{-1} , surpassing all other MOF-based anodes for LIBs (Fig. 3d)⁵². Increased electrochemical stability was also attributed to the small particle size, as swelling can be mitigated utilizing the interparticle space as a volumetric buffer region. This simple “pulverization” approach is highly promising and should be examined for other MOF systems. Similarly, smaller particles packed together constitute hierarchically porous MOFs where plentiful ion transport routes and short diffusion lengths result in superior cycling performance over monolithic MOF crystallites (Fig. 3e)⁵³.

MOFs as metal-ion cathodes: Despite the great interest in developing metal-ion anodes, cathode materials are the bottleneck for improving the performance of metal-ion batteries. LIB and SIB cathodes are typically transition metal oxides or metal phosphates, where the oxidation of the transition metal ion provides sites for Li^+ or Na^+ insertion (and reverse for discharging). MOFs as metal-ion cathodes are comparatively less developed than their anode counterparts. Most MOF cathodes utilize single-electron redox couples such as Fe(III)/(II) and Cu(II)/(I) , leading to low capacities ($< 100 \text{ mAh g}^{-1}$). Moreover, the poor electronic and ionic conductivity of MOFs translate to underutilization of redox-active centers buried in the bulk^{45,54}. However, emerging design strategies described in this review present a multitude of opportunities for MOF-based cathode materials. The chemical versatility of MOFs permit the incorporation of multi-electron redox-active metal nodes (e.g., Mn(IV)/Mn(II)) and linkers (e.g., quinones) to yield higher specific capacities, while MOFs with permanent porosity and large external surface area will improve electrode–electrolyte contact to enable more rapid charge conduction.

Design criteria and opportunities: As demonstrated, MOF metal-ion battery components can be improved by carefully selecting MOF attributes such as porosity, composition, morphology, and conductivity. Future MOFs designed for metal-ion batteries would significantly benefit from increased electron/ion storage capacity. This could be accomplished in MOF design, by installing redox-active metal or linker participants with a multitude of accessible oxidation states. The electronic and ionic diffusion length should also be minimized by utilizing high-surface area particle morphologies such as nano-sized or low-dimensional crystallites. Despite progress, MOFs face scrutiny as electrode materials for metal-ion batteries because of their low volumetric and gravimetric energy density compared to purely inorganic or organic material alternatives. However, the advances and strategies developed over the past 15 years demonstrate MOFs could have a place in next-generation metal-ion battery

technologies, especially with the rising demand for high-rate performance devices.

Lithium-sulfur batteries. Compared to LIBs, Li metal batteries boast significantly higher specific capacities of up to 3680 mAh g^{-1} , making them highly attractive for advanced energy storage devices⁵⁵. As the challenges of lithium metal anodes mirror our discussion of metal-ion batteries, we focus this section on how MOFs can enhance the performance of various cathode and separator materials in lithium-sulfur (Li-S) and lithium-selenium (Li-Se) batteries.

Lithium-sulfur batteries are a promising candidate of next-generation storage devices due to their high theoretical specific energy $\sim 2600 \text{ Wh kg}^{-1}$ and the low cost of sulfur⁵⁶. Distinct from metal-ion batteries, Li-S cathodes rely on the multi-electron conversion of elemental sulfur to polysulfides, boasting an extraordinary specific capacity of 1675 mAh g^{-1} S. During a typical discharge, elemental S_8 is reduced to soluble Li_2S_n ($n = 4–8$), before terminating at insoluble Li_2S_2 and Li_2S . A critical challenge for advancing Li-S batteries is their limited cyclability due to the “polysulfide shuttle” where soluble polysulfides can leach from the cathode and passivate electrode surfaces during cycling (Fig. 4a)⁵⁷. This phenomenon ultimately leads to severe capacity fading, high self-discharge rates, large internal resistances, and safety issues.

Physical encapsulation of polysulfides: MOFs are well suited for polysulfide encapsulation owing to their predisposition for stabilizing host–guest interactions. Their tunable pore geometries and apertures can facilitate ion diffusion, critical for fast charging and discharging (Fig. 4b)^{58,59}. In addition, the open and relatively flexible structures of MOFs can accommodate the large volumetric expansion of sulfur upon reduction to Li_2S . Addition of MOFs in Li-S cathodes are thus promising avenues for mitigating the polysulfide leaching.

Physical adsorption of polysulfides is intimately related to the pore structure of the MOF host. Typically, cage-like pores are more suitable than straight channels for sulfur encapsulation⁵⁹. The earliest reported MOF used for Li-S batteries is MIL-100(Cr) by Tarascon et al.⁶⁰ They employed a melt diffusion method to incorporate sulfur into MIL-100(Cr) pores in a composite cathode and observed increased capacity retention. The enhancement is attributed to the large cage-like pores and small windows (8.6 \AA) of MIL-100(Cr).

Chemical adsorption of polysulfides: Frameworks with coordinatively unsaturated metal sites can further increase their affinity with the negatively charged (poly)sulfide anions^{61–63}. Park et al.⁶¹ computationally explored 16 metal-substituted types of $\text{M}_2(\text{dobdc})$ for their anchoring ability of S_8 , Li_2S_4 , and Li_2S . Their calculations demonstrated that coordinately unsaturated metal sites are the dominant adsorption sites in MOFs. A study that compared MOF-525(2H), MOF-525(FeCl), and MOF-525(Cu) suggests that the number of Lewis acidic sites are important for binding to polysulfides⁶². MOF-525(Cu) with two open sites exhibited the best performance with a reversible capacity of $\sim 700 \text{ mAh g}^{-1}$ at 0.5C for 200 cycles (Fig. 4c). Other reports have similarly highlighted the relationship between open metal sites and capacity retention in MOF-based Li-S batteries, such as in HKUST-1^{58,63}, Mn MOFs⁶⁴, and Ni MOFs⁶⁵.

In addition, the organic linkers can also offer sites to improve sulfur–MOF interactions. Lithium polysulfides have been encapsulated within the pores of nMOF-867 with the assistance of sp^2 N atoms in organic linkers⁶⁶. Using a nMOF-867-based electrode, the battery showed outstanding capacity retention with little capacity loss over 500 cycles at a high current rate (Fig. 4d). Based on this study, more organic linkers with enhanced affinity for sulfur species are worth exploring.

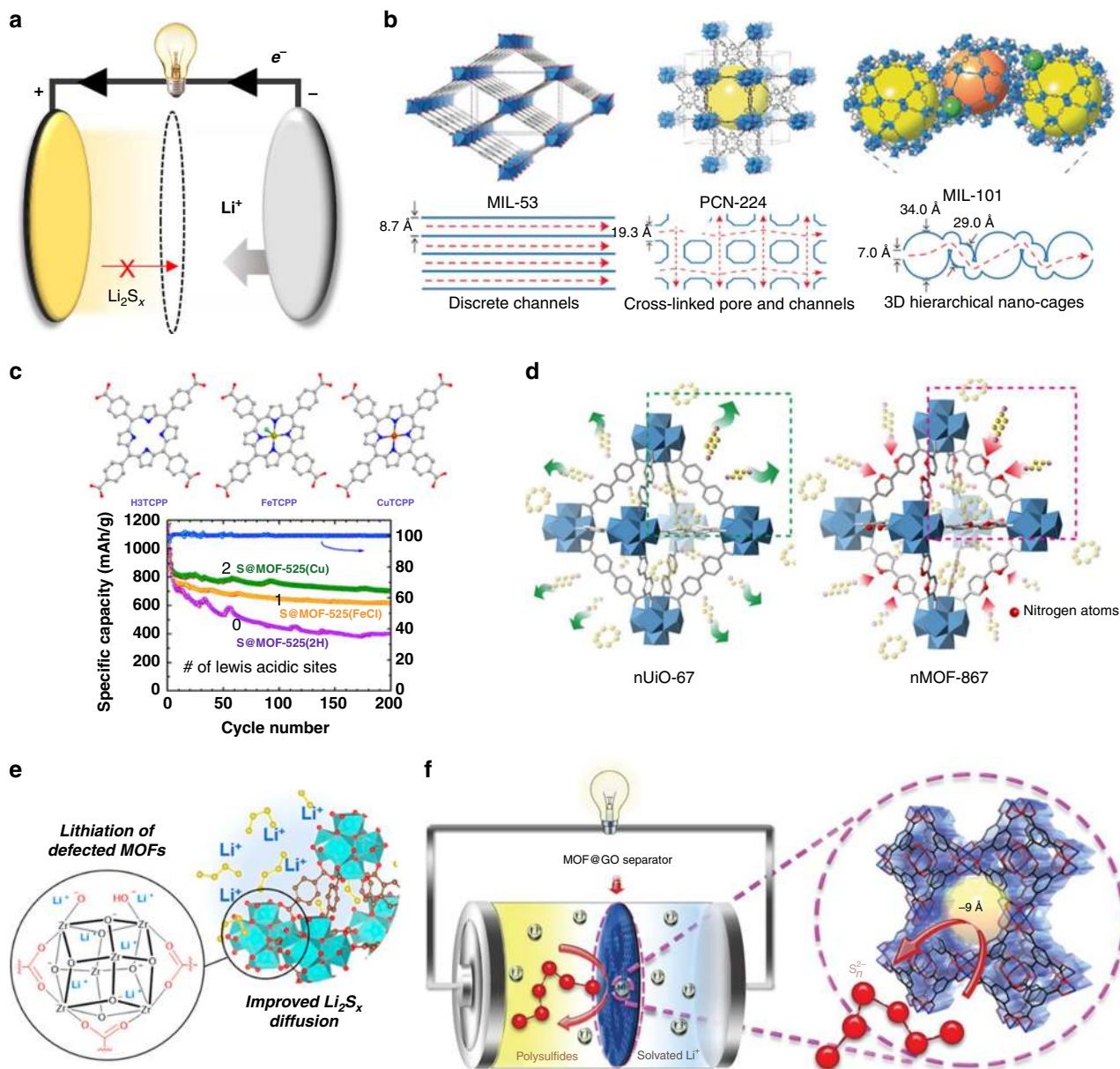


Fig. 4 Highlighted approaches using MOF chemistry to improve Li-S battery performance. **a** Li-S battery schematic including a separator between the electrodes. **b** Pore geometries and aperture sizes affect polysulfide encapsulation and charge transfer rate, where cage-like pores connected via channels show greater performance (adapted with permission from ref. 59 © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim). **c** Increasing the number of Lewis acidic metal sites available enhances chemical adsorption of polysulfides (adapted with permission from ref. 62 © 2015 American Chemical Society). **d** Tuning linker functionalities can provide more anchoring sites for polysulfides (adapted with permission from ref. 66 © 2016 Springer Nature). **e** Lithiation of MOF defects leads to enhanced ion conduction (adapted with permission from ref. 23 © 2019 American Chemical Society). **f** Micropores in MOF composite separators restrict polysulfide diffusion (adapted with permission from ref. 70 © 2016 Springer Nature)

Promoting charge transport: The insulating nature of S and Li_2S significantly limits effective utilization of active materials, requiring the use of conductive additives for electrical contact. Although most MOFs are not electronically conductive, framework-localized redox reactions have been accomplished using conductive additives. Such composites are multifunctional by combining the high-surface area and chemical tunability of MOFs with the conductivity of polymers and carbon materials. Moreover, the long-range order and high porosity of MOFs provide directional ion conduction, which can enable faster charge/discharge kinetics.

A recent report illustrated the power of multifunctional MOF composites for Li-S cathodes. In order to achieve both high

electronic and ionic conductivity, polypyrrole was crosslinked inside sulfur-impregnated MOFs to yield a MOF-polymer composite with conductivities 6–7 orders of magnitude higher than pristine MOFs⁵⁹. Of the three MOF composites tested, sulfur-impregnated PCN-224, a Zr-based MOF with porphyrin linkers, exhibited the best long-term battery performance with a specific capacity of 670 mAh g^{-1} and 440 mAh g^{-1} at 10C after 200 and 1000 cycles, respectively. The pore geometry of PCN-224 was speculated to decrease the ion diffusion length, while the large pore windows improved the ion transfer rate (Fig. 4b). Furthermore, the PCN-224 polymer composite also outperformed sulfur/polypyrrole controls, demonstrating the crucial role of the MOF for polysulfide confinement and long-term cycling.

Modulating the physical particle size and morphology of MOFs is another strategy to simultaneously enhance charge conduction and sulfur adsorption. Decreasing the particle size shortens the diffusion length, which promotes faster and more efficient conversion. For instance, the cycling performance of nano-sized ZIF-8 was significantly improved compared to other common MOFs with larger particle sizes⁵⁸. A “golden size” for ZIF-8 particles was subsequently identified to optimize both maximum capacity and capacity retention⁶⁷. As a general strategy, reducing MOF particle size or interpenetrating frameworks results in shorter diffusion lengths, improving ion and electron transport within the material^{59,68}.

Ion mobility can also be enhanced by introducing ion reservoirs in MOFs. UiO-66 functionalized with lithium *tert*-butoxide was shown to have two orders of magnitude higher ionic conductivity than the untreated MOF⁶⁹. Inspired by this improvement, our group explored strategies to construct a highly lithiated UiO-66 utilizing labile protons of defect sites (Fig. 4e)²³. The lithium content was found to correlate with improved ion conductivity. As a result, the MOF with the highest Li content, Li-UiO-66(50Benz), demonstrated a high specific capacity of 1272 mAh/g compared to 918 mAh g⁻¹ for the parent UiO-66 (50Benz) at a rate of C/10 (168 mA g⁻¹). The lithiated MOFs also show improved rate capabilities compared to non-lithiated MOFs, which further illustrate the role of lithiation for fast ion diffusion.

Li-S MOF separators: In addition to their utilization as cathode materials, MOFs have also been explored as separators in Li-S batteries. A MOF-based separator was developed as an “ionic sieve” for transporting Li ions while suppressing solubilized polysulfides from migrating to the anode. HKUST-1 was combined with graphene oxide (GO) to form a MOF@GO membrane with 3D channels and 9 Å-sized, ordered micropores (Fig. 4f)⁷⁰. Utilizing the MOF@GO membrane with a mesoporous, sulfur/carbon cathode, the fabricated batteries demonstrated enhanced cycling stability with a capacity fade of 0.019% per cycle over 1500 cycles. Recently, a comparative study of MOF-based separators, including Y-FTZB, ZIF-7, ZIF-8, and HKUST-1, demonstrated the factors that affect MOF stability and shuttle suppression during electrochemical cycling⁷¹. The batteries with Y-FTZB separators showed the best capacity retention of 557 mAh g⁻¹ after 300 cycles. The authors conclude that the high packing density of the Y-FTZB in the membrane is critical to prevent polysulfide diffusion. Crystallite morphology, size, and dispersity are thus additional parameters that can be optimized for MOF separators.

Extending Li-S strategies to Li-Se: Lithium-selenium batteries have attracted much attention recently because of their high theoretical volumetric energy density (~3253 mAh cm⁻³) and moderate gravimetric capacity (678 mAh g⁻¹)⁷². Compared to their Li-S counterpart, Li-Se batteries have shown improved rate and cycling performance as well as higher output voltage. Despite these advantages, Li-Se batteries are also faced with several major challenges. The Se cathode experiences huge volume expansion upon lithiation due to the lack of void space in its lattice structure. Although Se has a much higher electrical conductivity than S₈, the conductivity of cathode still needs further improvement to enhance ion/electron transfer. Similar to Li-S batteries, dissolution and shuttling of lithium polyselenides leads to low Se utilization and rapid capacity fading. As of yet, MOFs have only been used as a pyrolysis precursor to create porous carbon frameworks for Li-Se battery materials^{73,74}. However, the MOF strategies discussed for Li-S batteries should largely be transferable to Li-Se systems.

Design criteria and opportunities: MOFs have demonstrated potential as sulfur cathode hosts and separators in Li-S batteries.

Polysulfide anchoring and charge transport in MOF materials need to be optimized for further performance enhancement. Well-designed pore geometries are critical as cage-like pores are typically better for physical encapsulation of sulfur species than straight channels. Lewis acidity/basicity, coordinately unsaturated metal sites, and linker functionalities of MOFs are particularly important for chemical adsorption of sulfur species. MOFs with more Lewis acidic sites and N containing linkers show higher affinity for polysulfides. Aperture sizes also need to be carefully tuned to balance between sulfur retention and Li⁺/e⁻ transfer rate. Additionally, ions/electron diffusion lengths are affected by particle size of host materials, where smaller particle size favors high-rate charge transfer. Increasing the conductivity (ionic and electronic) of MOF hosts is another approach to achieve high-rate and high-capacity batteries. When utilized as separators, MOFs demonstrate advanced performance with fine-tuned crystallite morphology, well dispersed catalytically active sites and appropriate pore geometries. These design strategies are promising for further exploration of MOFs in Li-S/Li-Se batteries.

Lithium-oxygen batteries. Lithium-oxygen (Li-O₂) batteries, also referred to as lithium-air batteries, are typically made up of lithium metal anodes and porous carbon or composite cathodes where the ORR reaction occurs (Fig. 5a). In a typical discharge, reduction of O₂ in the presence of Li⁺ leads to the formation of lithium peroxide (Li₂O₂), avoiding the less reversible product lithium oxide (Li₂O)⁷⁵. This process yields a theoretical specific energy of ~2000 Wh kg⁻¹ for the entire cell. The efficiency and cyclability of Li-O₂ batteries are predominantly limited by the redox events at the cathode. Owing to the reactivity of O₂ and its reduced species, a number of side reactions can take place that limit cell lifetime and capacity retention. In addition, the reduction products Li₂O₂ and Li₂O are poorly soluble in organic electrolytes, passivating the cathode surface and making recovery of these species difficult upon charging. One approach to solve these problems is the use of a catalyst to facilitate electrochemical ORR and evolution (OER). MOFs have been well studied in heterogeneous catalysis for many different reactions including ORR and OER⁷⁶⁻⁷⁸, and their catalytic utility in Li-O₂ cathodes is just now being realized.

Incorporation of multifunctional catalytic frameworks in Li-O₂ cathodes: In a comparative study of various MOFs used as cathode materials in Li-O₂ cells, MOFs containing open metal sites exhibited outstanding specific capacities⁷⁹. For example, HKUST-1 and M-MOF-74 (M = Mg, Mn, Co) can achieve capacities between 4000 and 9420 mAh g⁻¹ compared to MOF-5, which had the poorest capacity at 1780 mAh g⁻¹ (Fig. 5b). Overall, the results suggest proper metal selection for catalysis is crucial for designing cells with high capacity. The authors also suggested the channel-like pores of MOF-74 contribute to increased accessibility of O₂ by the metal sites. In addition, it was found that smaller Co-MOF-74 particles greatly enhanced cell capacity due to shorter and more efficient O₂ diffusion pathways and a higher density of exposed active sites⁸⁰.

The synthetic tunability of MOFs is opportune for multifunctional catalytic systems. Bimetallic MnCo-MOF-74, which intrinsically contains open metal sites, was incorporated into Li-O₂ cathodes as a catalyst⁸¹. Homogeneous dispersion of the Mn and Co cations was found to be important for accessibility of catalytic sites by oxygen species. The bimetallic MOF allows the cells to achieve roughly double the cyclability of its monometallic analogs (from ~20 cycles boosted to 44 cycles) delivering 1000 mAh g⁻¹ at a current density of 200 mA g⁻¹. The authors explain that the Mn sites assist in the reduction of oxygen species while discharging, while the Co sites are able to efficiently reverse

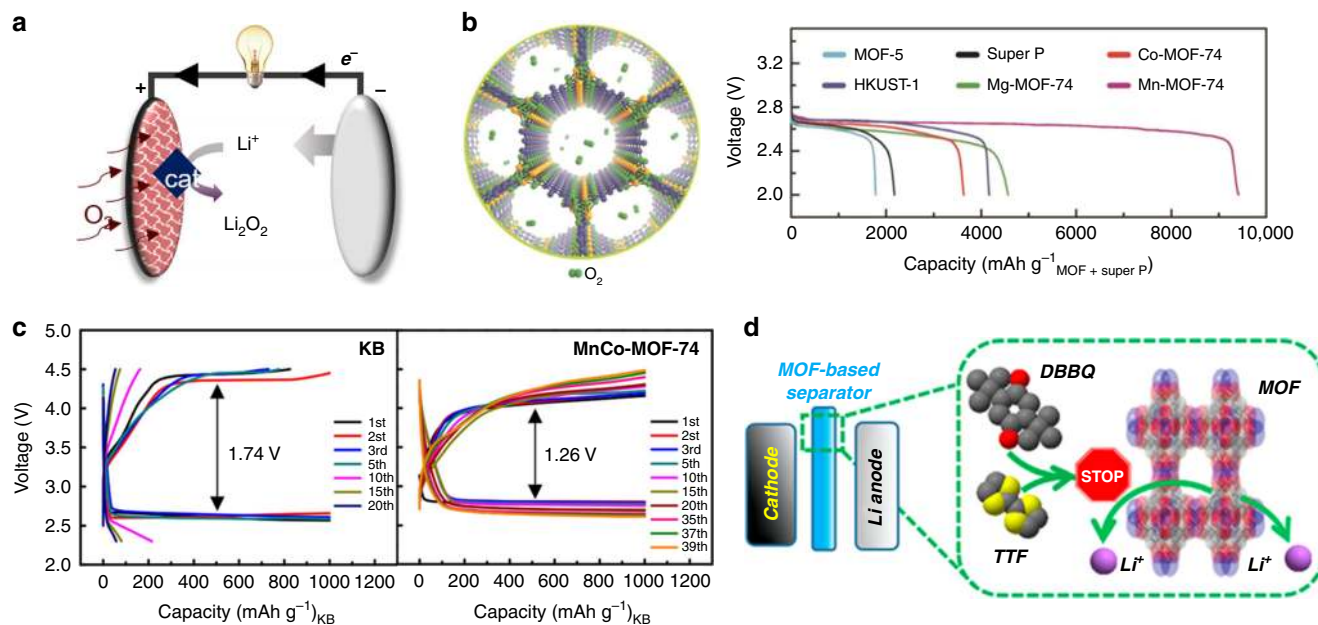


Fig. 5 Demonstrated MOF utility as electrode and separator materials in Li-O₂ batteries. **a** Schematic representing a typical Li-O₂ cell. **b** Use of select MOF catalysts in Li-O₂ cathodes to improve discharge capacity (adapted with permission from ref. ⁷⁹ © 2014 John Wiley and Sons). **c** Bimetallic, catalytic MOF cathode materials decrease overpotentials (compared to Ketjen Black) and extend Li-O₂ cell life (adapted with permission from ref. ⁸¹ © 2018 American Chemical Society). **d** MOF-coated separators protect Li anode to allow practical use of organic redox mediators at the cathode (adapted with permission from ref. ⁸² © 2018 American Chemical Society)

this process upon charging evidenced by reduced overpotentials (Fig. 5c). Together, the two metals enhance both efficiency and reversibility of discharge and charge processes, suggesting that multi-metallic MOFs with targeted catalytic activity are promising candidates for Li-O₂ cathodes.

Li-O₂ MOF separators: MOFs can also be used as separators to enable the use of organic redox mediators. Redox mediators permit more efficient ORR within the cathode architecture and prevent passivation/clogging of the Li-O₂ cathode (Fig. 5d)⁸². However, these molecules react with the lithium anode and diminish the deliverable capacity and cyclability. To resolve this issue, a film of HKUST-1 was grown on a Celgard separator to prevent the mediator from diffusing to the Li anode, allowing the battery to maintain cell function for over 100 cycles⁸². Separators are a promising application for MOFs, and future work on MOF separators should consider including Li⁺ conduction pathways to decrease mass transport resistance.

Design criteria and opportunities: Overall, Li-O₂ batteries show promise for providing high-capacity energy storage to meet future energy consumption needs, and MOFs are outstanding materials to catalyze development of this technology. Still a very nascent field, MOFs for Li-O₂ batteries should aim to address limitations to catalysis, ion transport, and pore structure modification. Future MOFs designed for Li-O₂ cathodes should possess open metal sites for catalysis, ideally using multiple metal species for optimized ORR and oxidation. However, care should be taken to ensure that the catalyst aids with favorable Li-O₂ reactions, rather than degradation of other organic species which may appear at the same voltages. Multi-metallic MOFs can be achieved during synthesis of the framework or through post-synthetic modification. Defect engineering has yet to be utilized for MOF catalysis in Li-O₂ systems, but would be a promising method for enhanced porosity and catalytic activity. Both crystallite and pore morphologies should also be considered in the MOF selection to optimize delivery of O₂ to active redox sites. We envision MOFs capable of gas separation and storage selective to O₂ would also be useful for Li-O₂ batteries to prevent adverse

reduction of H₂O and CO₂ in non-aqueous electrolyte systems when air is the source of oxygen.

Supercapacitors. Supercapacitors, or electrochemical double layer capacitors, operate by a voltage-driven accumulation and release of ions at electrode–electrolyte interfaces (Fig. 6a). The energy in a supercapacitor is stored in the electrostatic separation of charged ion pairs at the electrode surface, rather than through electrochemical conversion as in a battery. Therefore, free from the limitations of redox kinetics, supercapacitors exhibit superior cycling efficiency, device lifetime, high specific power, and rapid (dis)charging. Given that energy storage occurs only at the surfaces of the electrodes, porous electrode materials with high-surface areas are necessary.

Optimizing accessible surface area: Intrinsic crystallinity and high porosity render MOFs ideal for improving supercapacitor performance. The extensive synthetic control over MOF crystal structure, morphology, particle size, and surface composition provides a unique handle for combatting pore limitations and improving contact with the electrolyte. A comparative study of 23 nanocrystalline MOFs (nMOFs) demonstrates the utility of MOF-graphene electrodes for supercapacitors⁸³. The reduced particle sizes of nMOFs are ideal for creating high-surface area electrodes with short diffusion paths. A device utilizing nMOF-867 was shown to achieve a specific capacitance of 726 F g⁻¹ (Fig. 6b). The MOF was postulated to enhance charge storage by providing polar sites in the bipyridine linker for interacting with the separated ions. Similarly, supercapacitors that contained smaller UiO-66 particles exhibited significantly higher charge storage than those with larger particles⁸³. For example, particle sizes of ~100 nm in diameter achieved a specific capacitance of 1144 F g⁻¹ at a scan rate of 5 mV s⁻¹ while the largest particle size of 400 nm was a mere 207 F g⁻¹.

Controlling preferred crystalline facets can also dramatically improve storage capabilities, particularly in MOFs featuring pseudo-capacitive behavior. A layered Ni-BDC MOF with

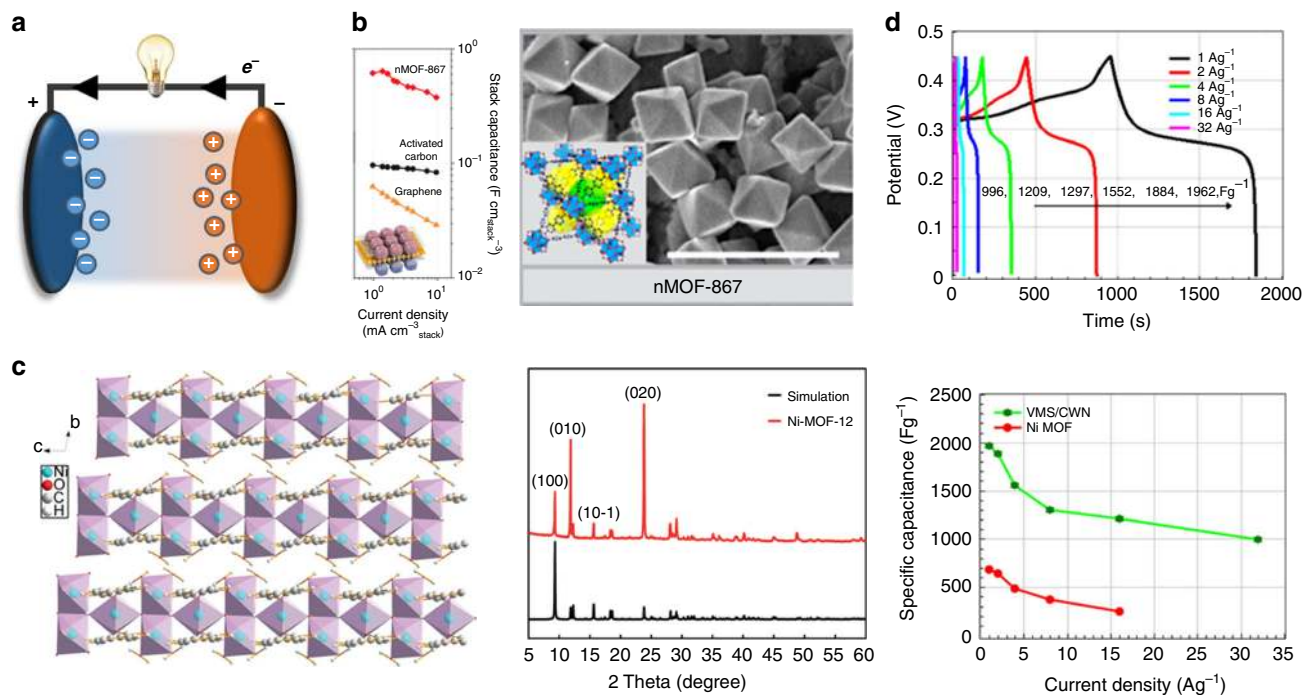


Fig. 6 Strategies employing MOFs within supercapacitor devices. **a** Schematic illustrating separation of charges to the polarized electrodes in a typical supercapacitor. **b** Use of nanocrystalline MOF electrode materials for greater capacitance; scale bar = 500 nm (adapted with permission from ref. ⁸³ © 2018 American Chemical Society). **c** 2D MOFs with preferential crystalline facets optimize use of electrode surface area (adapted with permission from ref. ⁸⁴ © 2014 Royal Society of Chemistry). **d** Vertically arranged MOF nanosheets make active electrode surface area more accessible for increased capacitance (adapted with permission from ref. ⁸⁵ © 2018 Springer Nature)

preferential exposure of (100) facets was employed as a supercapacitor electrode (Fig. 6c)⁸⁴. The devices tested were shown to have specific capacitance of 1127 F g⁻¹ at a charge rate of 0.5 A g⁻¹, over 90% of which was retained over 3000 cycles. The higher concentration of exposed Ni atoms on the (100) facet was postulated to improve the performance by providing additional redox sites and enhancing ionic conductivity. Similarly, highly ordered Ni-MOF nanosheets with directionally controlled growth on a carbon support exhibited a specific capacitance of 1962 F g⁻¹ at a current density of 1 A g⁻¹ (Fig. 6d)⁸⁵. After 1200 cycles, 97% of the specific capacitance was retained. Furthermore, pushing the current to 32 A g⁻¹, the device still produces a specific capacitance of 996 F g⁻¹. The controlled morphology in this electrode material allows for greater pore accessibility, which boosts device performance. Together, these examples of MOFs with precise crystallographic control demonstrate yet another advantage of using frameworks for energy storage devices.

Design criteria and opportunities: Supercapacitor electrode materials must have particular properties suited to both the electrolyte and operational conditions of the device. MOFs provide the variability and synthetic control to fine-tune these properties such as pore size, particle dimensions, and ionic conductivity to create reliable electrode materials. For ongoing work in this field, the MOF pore size relative to the effective diameter of the selected electrolyte ions should be optimized, as this will greatly impact the transport of ions (with or without their respective solvent shells) within MOF pores and determine device capacitance. Similarly, pores should be made more accessible by reduction of particle size or exploration of high-surface area morphologies (defects, hierarchically porous MOFs, etc). Electrode materials should be thermally and electrochemically stable within the operational conditions, as certain MOFs have been observed to dissolve under reductive potentials^{86–88}. Finally, a few conductive MOFs have been tested in

supercapacitors^{89,90}, demonstrating early promise and room for development to circumvent the need for conductive carbon additives. Ultimately, the inherent chemical and physical control and high porosity make MOFs highly advantageous for developing novel supercapacitor materials.

Promising future directions

The discovery of new materials is absolutely critical for the development of advanced energy storage devices. This section outlines bottlenecks in frontier technologies in which MOFs are uniquely suited to address (Fig. 7).

Solid-state electrolytes. Traditional battery electrolytes are composed of flammable organic solvents, posing safety risks and reliability concerns for high energy density batteries. Replacement of solution electrolyte with solid-state electrolytes is of great interest. Candidate materials must have high ionic conductivity (above 10⁻⁴ S cm⁻¹ at room temperature) and an ideal Li⁺ transference number (stationary anion, only cation mobile). In addition, solid-state electrolytes must be electronically insulating to prevent shorting the battery and be mechanically and chemically robust with a reasonable operating temperature and electrochemical window.

Solid-state inorganic materials are attractive candidates as they can have high ionic conductivities (as high as ~10⁻² S cm⁻¹ at room temperature) and can operate within a large thermal and electrochemical window. However, their brittleness and poor chemical stability under processing conditions limit their utility. Furthermore, the lack of structural and atomistic control from top-down syntheses prevent rational materials design. MOFs, on the other hand, can potentially access good ion mobility from soft chemical interactions, solvent incorporation, and open channels. In addition, MOFs are more compatible with carbon-based

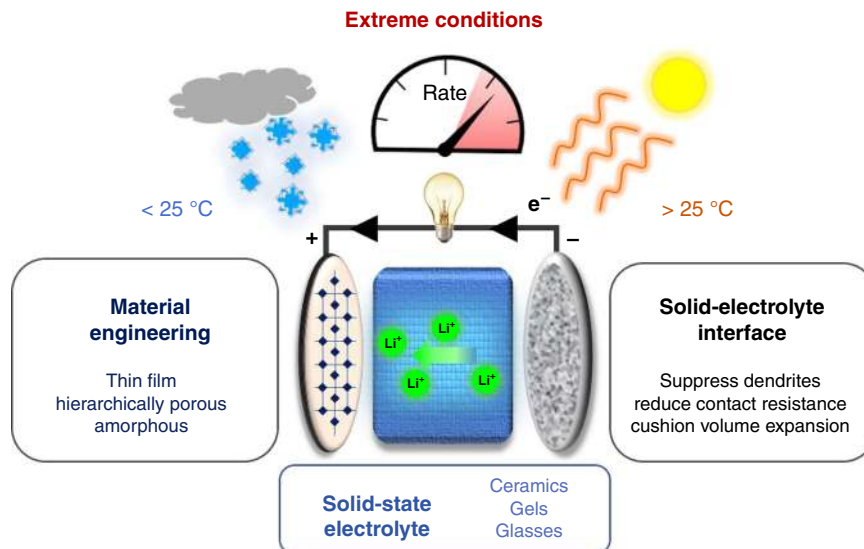


Fig. 7 Promising applications for MOFs to advance energy storage technologies MOFs are well suited to meet performance demands for high power devices, operation in extreme conditions, stabilizing the solid–electrolyte interface, and even serving as the electrolyte

electrodes than solid inorganic compounds. MOFs have been suggested for solid electrolytes previously^{25,69,76,91} but have been scarcely employed in full device testing⁹².

Gel electrolytes are also promising materials owing to high ionic conductivity and ease of preparation. However, they have limited electrochemical stability under the high voltage and charge rate requirements of advanced energy storage devices. Gel polymers generally consist of ether, amine and ionic groups that facilitate in solvating ions for charge conduction. Such functional groups have already been incorporated into MOFs intrinsically or via post-synthetic modification^{93,94}. An anionic framework obtained either through the use of tethered anionic functional groups or engineered anionic defect sites may similarly increase the ion transference number and positively impact rate capability.

Electrode–electrolyte interfaces. MOFs can be utilized to stabilize the solid–electrolyte interface (SEI). In a battery, a native SEI is formed on the surface of the electrode from the deposition of the decomposed electrolyte components. This passivating layer generally protects against further degradation, but continuous cycling damages the SEI. An introduced MOF SEI can address these issues by preventing electrolyte decomposition, promoting ion transport, and accommodating volumetric changes. For example, there are several reports of using MOF coatings on Si anodes in LIBs^{95,96}. The addition of the MOF coating improved cyclability by offering a protective “cushion” for volume expansion as well as by lowering the cell resistances and promoting ion conduction in the electrolyte-filled MOF. MOF separators on top of Li metals have also been demonstrated to encourage even Li deposition to prevent dendrite formation⁹⁷. Still in its infancy, the application of MOFs as protective layers will require ionically conductive and robust materials as well as the identification of compatible synthesis and deposition techniques upon the electrode surface. The multi-faceted nature of MOFs allows researchers to use varying in operando, in situ, and ex situ characterization techniques to study electrolyte and SEI chemistries.

Battery operation in extreme conditions. High power applications, such as batteries for electric vehicles, necessitate rapid delivery of energy in a short period of time and intermittent usage. At the large applied currents during charge/discharge,

battery materials must have fast charge transfer kinetics, low contact resistance, and abundant transport pathways to carry out redox reactions. Moreover, high-rate batteries present serious safety issues as improper choice of materials can result in cell damage via dendrite formation, volumetric expansion, and thermal runaway. To counteract these concerns, flexible and durable MOFs can accommodate structural changes of cell components to inhibit dendrite growth and maintain electrode contact. In addition, their open channels can be infiltrated with electrolyte to diminish large ion concentration gradients.

In addition to demanding charge rates, there is also a growing need for energy storage devices to reliably deliver power in extreme environmental conditions. Reliable energy storage is needed in hot and cold climates on Earth and in space (−60 to 150 °C) while aeronautical applications may have different temperature and pressure requirements. However, current battery technologies are often unsafe and unreliable when these environmental limits are pushed. For instance, the use of flammable electrolytes under increased temperatures can lead to catastrophic cell failure, while cells operating at low temperatures face severely limited power output primarily due to sluggish mass and charge transport.

Owing to their thermal and mechanical stability, MOFs used as solid-state electrolytes or separators may expand the limits of battery technology to function safely and proficiently in extreme conditions. The electronically insulating nature of most MOFs, in combination with tunable porosity and ionic conductivity, make them natural fits to act as battery separators. Catalytic MOF cathode materials or additives may also expand thermal operation ranges of batteries, for example, by reducing the charge transfer barriers at low temperatures or controlling reactions to prevent runaway at higher temperatures.

Engineering MOFs for device components. A large number of the devices discussed in this review employ MOF composite slurries, which can have limited charge conduction pathways. To address this, improved interfacial contact can be obtained using deposition methods to form uniform MOF films. Direct deposition onto a substrate ensures homogeneity and precise control of layer thickness. Furthermore, the ability to use soft materials like polymers as substrates will permit emergent flexible electrodes. As direct deposition techniques have been explored from other

classes of materials, design strategies from devices and processes that employ polymers, porous carbons and metal-oxides will likely find applicability in MOF-based devices.

The vast opportunities for new functionalities in MOFs have led to efforts to create frameworks with ordered structures at meso- and macroscale lengths^{98–100}. Crystallographic control of MOF components can enhance porosity and availability of metal sites, ultimately benefitting device performance. New physical properties of synthesized MOFs will also expand their applications in energy storage devices. Amorphous MOF gels and glasses have recently gained interest^{101–105}. In particular, they show promise as novel transparent materials that possess favorable MOF properties. Glasses and gels generally do not exhibit large grain boundary resistances, are less brittle, and can be geometrically shaped. Thus, amorphous MOF materials may fill a new niche in electronic applications where enhanced flexibility, transparency, and high charge mobility are priorities.

Outlook

Our review has highlighted some of the most promising strategies for employing MOFs in electrochemical energy storage devices. The characteristic properties of MOFs—porosity, stability, and synthetic tunability—provide ample design criteria to target specific bottlenecks in electrode and electrolyte development. Future identification, utilization, and development of strategies to promote charge storage and transport will set MOFs apart from porous carbons, polymer, and inorganic materials.

Despite their potential, there is still much to be learned about effective applications of MOFs in energy storage devices. Design strategies employed in polymers, carbons, ionic liquids, and solid inorganic compounds can serve as inspiration for identifying and discovering new MOF architectures for superior storage capabilities. Furthermore, MOF composite materials are vastly underexplored and their investigation will likely reveal new parameter space at the intersection of conventional soft/hard materials and MOFs. Fundamental and applied knowledge gained from MOF-based devices will thus be invaluable for designing next-generation materials for emerging technologies in flexible and transparent electronics, solid-state electrolytes, and advanced energy storage devices in moderate and extreme environments.

Received: 12 March 2019 Accepted: 17 June 2019

Published online: 26 July 2019

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Acknowledgements

We thank the Department of Chemistry and Johns Hopkins University for graduate student support and start-up funding. A.E.B. and D.A.B. both received Harry and Cleio Greer Fellowships from the Department of Chemistry. A.E.B. also thanks the ARCS Foundation for the Metropolitan Washington Chapter Scholar Award.

Author contributions

A.E.B., D.A.B. and B.L. conducted the literature search. A.E.B. and D.A.B. equally contributed in writing the majority of the main text, while B.L. wrote a section of the main text. V.S.T. facilitated in the writing and editing of the main text.

Additional information

Supplementary information accompanies this paper at <https://doi.org/10.1038/s42004-019-0184-6>.

Competing interests: The authors declare no competing interests.

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