

Review

Recent Progress in Metal-Organic Framework-Derived Chalcogenides (MX; X = S, Se) as Electrode Materials for Supercapacitors and Catalysts in Fuel Cells

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Abstract: Supercapacitors (SCs) are recognized by high power densities and significantly higher cyclic stability compared to batteries. However, the energy density in SCs should be improved for better applications and commercialization. This could be achieved by developing materials characterized by such porous structures as metal-organic frameworks (MOFs) and metal chalcogenides in the electrodes' materials. Herein, the recent advances in MOF derived from metal sulfides and selenides as electrode materials for SCs are reviewed and discussed. Strategies such as adopting core-shell structures, carbon-coating, and doping, which are used to promote the electrochemical performances of these MOF-based materials, are presented. Additionally, the progress in developing S-doped MOF-derived catalysts for the oxidation-reduction reaction (ORR) in the cathode of fuel cells is also reviewed. In addition, the challenges and future research trends are summarized in this minireview.

Keywords: metal-organic frameworks (MOFs); supercapacitors (SCs); sulfides; selenides



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1. Introduction

Batteries such as Li-ion and Zn-air are characterized by high energy density but low power density and short cycle life. Meanwhile, when compared to batteries, supercapacitors (SCs) exhibit lower energy density but higher power density, operate safely, have higher cyclic stability, lower cost per cycle, lower internal resistance, and higher efficiency [1,2].

SCs consist of two electrodes, namely an anode and a cathode, and an electrolyte in between. The electrodes are assorted as capacitive electrodes made of carbon materials such as activated carbon (AC), carbon nanotubes (CNTs), graphene, and pseudocapacitive electrodes made of materials such as RuO₂ and MnO₂. The charge/discharge mechanism of the capacitive electrodes depends on the fast arrangements of the charges; it does not include redox reactions since the latter utilizes Faradic processes associated with redox reactions [3].

If the SC consists of two identical capacitive electrodes, it is called an electric double-layer capacitor (EDLC). The naming is ascribed to the formation of a double layer at the electrode-electrolyte interfaces as the spontaneous charges' rearrangement occurs when the electrically conductive electrodes are immersed in an ionically conductive electrolyte [4,5]. On the other hand, if the anode and cathode are identical pseudocapacitive electrodes, it is then called a pseudocapacitor. Unlike EDLCs, pseudocapacitors depend on Faradic processes that are associated with redox reactions. These reduction/oxidation reactions occur at or near the surface of the pseudoactive electrode materials, where electrons transfer induces a change in the valence state of the active material [6,7]. EDLCs

render higher power density, while pseudocapacitors have higher energy density [8,9]. To exploit these two properties, researchers came up with hybrid asymmetric supercapacitors (ASCs) comprising a capacitive electrode and a pseudocapacitive electrode. However, the imbalance between the charge/discharge kinetics of the two electrodes reduces the overall efficiency of the ASC. To overcome this mismatch and obtain a wider operating potential window (OPW), researchers developed ASCs with two different pseudocapacitive electrodes [3].

Enhancement of the electrochemical performance of the ASCs depends significantly on the performance of the electrodes, which in turn depends on the selected materials and their morphological structure. For example, improving the electrochemical performance of a pseudocapacitive electrode could be achieved by increasing the ion-accessible electroactive surface area and avoiding aggregation of the nanomaterials.

Metal-organic frameworks (MOFs) are promising porous crystalline materials consisting of metal ions and organic ligands linked to them via coordination bonds, such as auxiliary hydrogen bonds and metallic bonding resulting in van der Waals force interaction [10,11]. MOFs have several advantages over conventional porous materials, including diverse scaffold structure, tunable pore size, large specific surface area (SSA) ranging from 1000 to 10,000 m²/g [12], high thermal stability, and abundant active sites [13]. With these features, MOF-based electrodes and MOF-derived electrodes (MOF is used as a sacrificial precursor to produce the electrode's materials) have attracted attention in the ASCs research field [14–16]. Although the preparation of MOF-derived materials is considered an energy-intensive process, MOFs and MOF-derived materials are still attractive in energy storage applications due to the aforementioned properties [17–19]. Meanwhile, transition metal chalcogenides (TMCs), i.e., sulfides and selenides, have received significant attention in the supercapacitors research field [20,21] because of their tunable stoichiometric compositions, exclusive crystal structures, abundant redox sites, and relatively higher electrical conductivity than their corresponding metal oxides. When MOFs are transformed into the sulfide and selenide form through anion exchange [22,23], they retain the shapes of the pristine MOFs, which have a high porosity [24]. Therefore, ASCs with superior electrochemical performance could be achieved by synthesizing electrodes with MOF-chalcogenide-based materials.

MOF-derived materials also demonstrated superior performance when used as catalysts for oxygen reduction reaction in the cathode electrode in the fuel cells (FCs) [25]. Fuel cells convert the chemical energy of the fuel onto electrical energy. This process involves an oxidation reaction in the anode where the produced ions transfer to the cathode through the membrane while the electrons transfer to the cathode side through an external circuit. In the cathode, a reduction reaction takes place. In proton-exchange membrane fuel cells (PEMFCs) [26], direct methanol fuel cells (DMFCs) [27,28], direct ethanol fuel cells [29], direct urea fuel cells [30], direct and microbial fuel cells (MFCs) [31,32], the electron acceptor in the is oxygen i.e., oxygen reduction reaction (ORR) occurs in the cathode. The efficiency of the ORR depends significantly on the type of the utilized catalyst because the ORR has a slow reaction kinetics [33,34]. The commonly used catalysts, platinum and its noble-metal-based alloys, have drawbacks of very high cost, low durability, and insufficient methanol tolerance [35,36]. Due to the aforementioned advantages of MOF-derived materials, such as high porosity, which allows for facilitated electron transport and increased density of active sites, they have been attractive as non-noble metal catalysts for ORR.

Herein, we review the recent development of metal-organic framework-derived metal chalcogenides (MX; X = S, Se) as electrode materials for supercapacitors and as catalysts for fuel cells, especially for the ORR in the cathode. This review paper is different than other similar ones available in literature as (1) it is not limited to a certain type of MOFs/linker such as zeolitic imidazolate framework-67 (ZIF-67) [37]; (2) unlike reviews [13,18], this review mainly focuses on MOF sulfides and selenides and excludes papers that focus on oxide, hydroxides, and phosphides; and (3) the selected papers used in this review are recent

ones published starting from 2017. Furthermore, this review introduces a comprehensive discussion of the recent work reported in this field.

Before reviewing the metal sulfides and selenides MOF-based materials for supercapacitors and fuel cells, it is important to discuss the fundamental electrochemical characterization techniques and parameters used to evaluate the effect of utilizing these materials on enhancing the performances of supercapacitors and fuel cells.

1.1. Characterization of the Electrodes and Supercapacitors' Performances

The performance of the newly developed electrodes and the completely assembled asymmetric SC device can be characterized through electrochemical measurements. For the individual electrodes, the electrochemical measurements are normally conducted using the three-electrode setup in an electrolyte solution. The solution could be an aqueous or non-aqueous [38], an alkaline (like KOH solution), acidic (like H₂SO₄ solution), or neutral solution (like NaNO₃ solution), whereas testing the performance of the full asymmetric SC can be carried out using the two-electrodes configuration. These tests include cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), electrochemical impedance spectroscopy (EIS), and stability tests. The following equations are used to calculate the electrochemical parameters:

$$E_{device} = E_{positive} - E_{negative} \quad (1)$$

where E_{device} , $E_{positive}$, and $E_{negative}$ refer to the potentials of the SC (device), the positive electrode, and the negative electrode, respectively.

The capacitance of a capacitive electrode C (Farad) estimates its capability to store charge

$$C = \frac{\Delta Q}{\Delta U} \quad (2)$$

where ΔQ is the stored charge and ΔU is the voltage applied on the electrode [3]. On the other hand, if faradic reactions are involved in the storage mechanism, then we calculate another parameter which is capacity.

The areal capacity of the device, C (similar notation as capacitance, but the unit is different), can be calculated from the GCD result using the equation:

$$C = \frac{I \times t}{3600 S} \quad (3)$$

where C is the areal capacity (mA h cm⁻²), I is the constant current (mA), t is the discharge time (s), and S is the area of the electrode material (cm²). The reader would notice that most of the publications reviewed here calculated the capacity, not the capacitance; this is because the electrodes they fabricated are pseudocapacitive electrodes, not capacitive electrodes.

The specific energy density E (W h Kg⁻¹) of the asymmetric SC can be calculated using the equation:

$$E = \frac{I}{m \cdot 3.6} \int V dt \quad (4)$$

where m is the mass of the active material, and V is the potential range.

The specific power P (W Kg⁻¹) of the asymmetric SC can be determined using the following expression:

$$P = \frac{E \times 3600}{t} \quad (5)$$

1.2. Characterization of the Catalysts and Fuel Cells' Performances

The catalyst's electrochemical performance is tested using the three-electrode configuration with the catalyst in the working electrode, reference electrode, and counter electrode. The working electrode is usually a glassy carbon electrode (GCE) with the catalyst ink deposited on it. The ink is a mixture of the prepared catalyst, binder (Nafion),

and solvent (like ethanol or isopropanol). The testing medium can be acidic or alkaline depending on the targeted application (type of fuel cell) selected by the researchers. The electrochemical performance of the synthesized electrodes is examined through CV, linear sweep voltammetry (LSV), chronoamperometric (CA), and accelerated degradation test (ADT).

The effect of the new catalyst on the performance of the fuel cell is tested using the two-electrode method. The synthesized catalyst is used for ORR. The cathode, the electrode at which the ORR usually takes place, is prepared by casting the ultrasonicated catalyst ink on carbon paper or carbon cloth. The anode, membrane, and cathode are then pressed together to form the membrane electrode assembly (MEA), which is placed between current collectors and examined under real fuel cell operation.

2. Metal Sulfides in Supercapacitors

Transition metal sulfides are considered promising for SC electrode materials due to their higher electrochemical activity and superior electrical conductivity than other metal oxides or hydroxides [14,39]. Because of the lower electronegativity of sulfur compared with that of oxygen, sulfides tend to have more flexible structures and enhanced electron transfer compared with those of oxides [24]. There are three main methods to obtain sulfurized MOF-based materials: (1) the hydrothermal method in the presence of a sulfurizing agent such as thioacetamide (TAA), thiourea, or sodium sulfide; (2) refluxing the precursor in the presence of the sulfurizing agent at relatively low temperature; and (3) direct carbonization of the MOF or its derived oxide/hydroxide in the presence of sulfur powder under inert atmosphere at relatively higher temperatures [40].

To design wearable energy storage devices, research work focusing on fabricating flexible electrodes has been performed by synthesizing electroactive materials such as sulfurized MOFs on flexible substrates such as carbon cloth (CC). For such an application, the electrode should render very high stability by retaining a high performance even after thousand times of bending the electrode or the device. For example, Tao et al. [41] fabricated a flexible binder-free ASC using CC as the substrate. The active material in the positive electrode was nickel-cobalt bisulfide (NiCoS) nanosheet arrays, which were synthesized by depositing 2D MOF Layered double hydroxides (LDH) precursors on the CC skeletons. The LDH precursors were converted onto NiCoS by sulfidation through an ion exchange route (the sulfurizing agent was $\text{Na}_2\text{S} \cdot 6\text{H}_2\text{O}$). Figure 1 shows the field emission scanning electron microscopy (FESEM) images and the corresponding energy-dispersive X-ray spectroscopy (EDX) images of the NiCoS/CC, in addition to the FESEM images of the precursors (Co-MOF/C and NiCo-LDH/CC). By comparing Figures 1d–f and 1g–i, which correspond to the NiCo-LDH/CC precursor and the NiCoS/CC, respectively, it is clear that the NiCoS/CC integrally inherited the nanoarray structure of NiCo-LDH/CC precursor, which appears with a rough, porous surface that is well distributed on the CC substrate. Furthermore, the electrical and mechanical attachment of the nanosheets to the skeletons was robust, leading to enhanced electrochemical characteristics (see Table 1 for the values of the electrochemical parameters). With regard to the storage mechanism of the NiCoS/CC electrode, sufficient interspace for electrolyte penetration was induced by the direct growth of the NiCoS nanosheets on the CC substrate. Furthermore, the roughness and porosity of these nanosheets allowed for bigger areas of contact with the electrolyte and hence facilitated the diffusion of the electrolyte ions to the interior surface of the active material. The strong adhesion between the NiCoS nanosheets and the CC skeletons and the fact that this electrode is binder-free explains the accelerated electron transfer during the charge/discharge process. A hybrid ASC was fabricated using the NiCoS/CC as a positive electrode and activated carbon (AC) as a negative electrode. The device manifested high capacitance, high energy density, high cyclic stability, and significant mechanical stability, making it a good candidate for next-generation wearable devices.

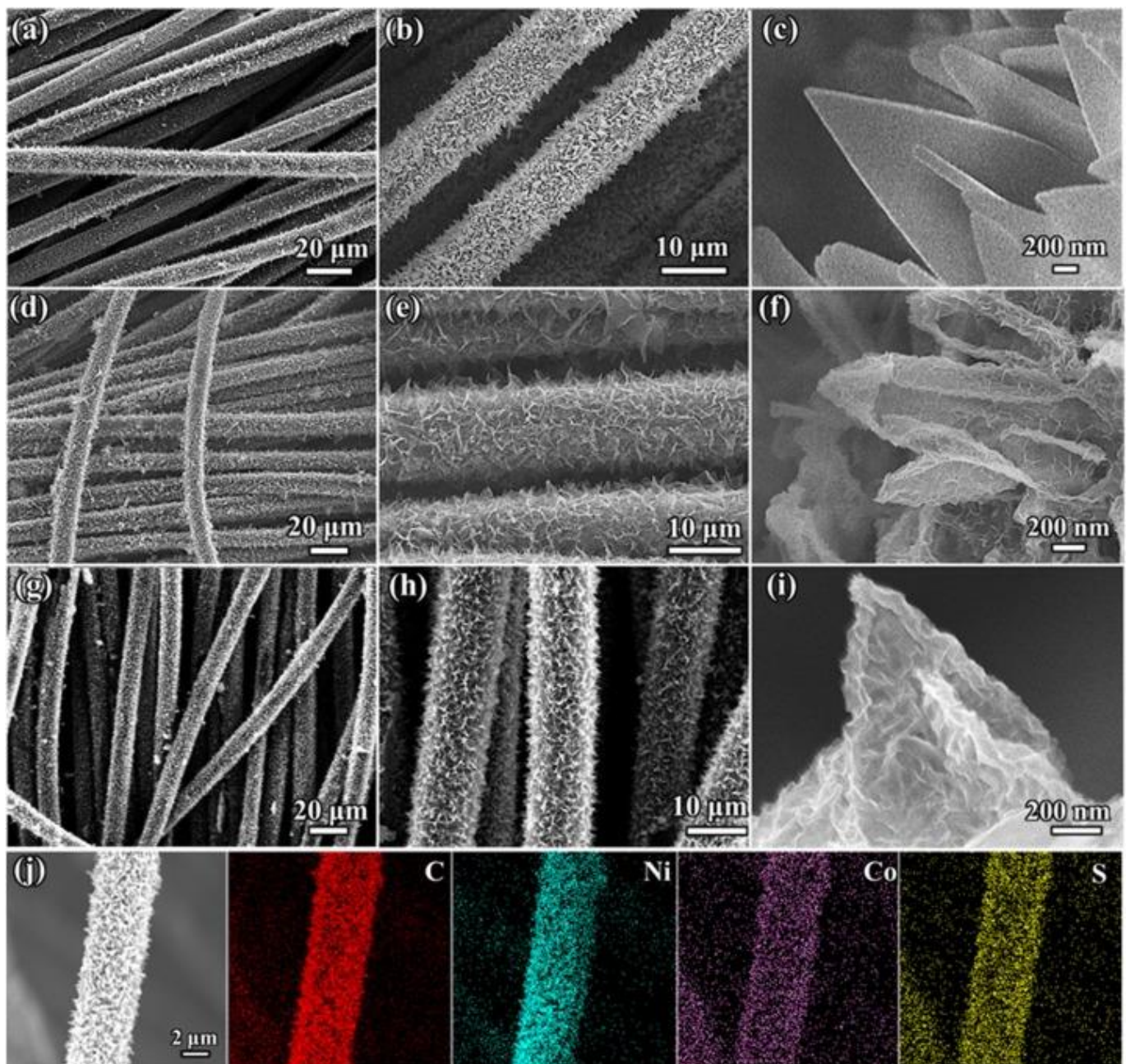


Figure 1. FESEM images of (a–c) Co-MOF/CC, (d–f) NiCo-LDH/CC, and (g–i) NiCoS/CC. (j) ping images of NiCoS/CC [41]. Copyright 2020 Elsevier.

Elemental Map

Similarly, Wei et al. [42] fabricated bimetallic sulfurized core-shell MOF-based electrodes for high-performance flexible asymmetric supercapacitors. The core for both positive and negative electrodes was zinc-cobalt sulfide nanosheet scaffolds (ZnCoS-NSs). The Zn-Co MOF arrays were fabricated on a carbon cloth substrate at room temperature and then sulfurized using a hydrothermal anion-exchange reaction with Na_2S as the sulfurizing agent. The ZnCoS-NSs possessed high electric and ionic conductivity and worked as a 3D platform for the stable growth of additional active materials. The shell of the positive electrode was nickel hydroxide $\text{Ni}(\text{OH})_2$, ending up with a pseudocapacitive positive electrode $\text{Ni}(\text{OH})_2@\text{ZnCoS-NS}$ that exhibited a very high capacitance of 8.1 F cm^{-2} at a current density of 3 mA cm^{-2} . On the other hand, a vanadium nitride (VN) shell was synthesized over the ZnCoS-NSs core using the solvothermal method to obtain the nega-

tive electrode VN@ZnCoS-NS with a high capacitance of 1.35 F cm^{-2} at a current density of 3 mA cm^{-2} . A flexible ASC was fabricated using the designed two electrodes and a PVA/KOH electrolyte. The ASC $\text{Ni(OH)}_2\text{@ZnCoS-NSs} // \text{VN@ZnCoS-NS}$ manifested a high specific capacitance of 210.7 F g^{-1} at a current density of 0.5 A g^{-1} , high energy density of 75 W h kg^{-1} at a power density of 0.4 kW kg^{-1} , high cycling stability (around 82% capacitance retention after 10,000 cycles), and superior flexibility by retention of ~92% of the initial capacitance after bending for 4000 times. The outstanding performance was attributed to: (1) the direct growth (binder-free) of the ZnCoS-NS on the CC current collector ensured their strong adhesion to each other, creating a short path for charge transfer. (2) The ductile crystal structure of the ZnCoS-NSs scaffold worked as a mechanical buffer that incurs the volume change of the active materials during charge/discharge; hence, it efficiently protects the core-shell structure from deformation and fragmentation. (3) The shells (Ni(OH)_2 nanoflakes and VN nanoparticle coating) were directly and homogeneously grown on the ZnCoS-NSs surface, which endows assessable active sites for contact with the electrolyte. This leads to a short diffusion path during the electrochemical reactions. (4) Using the VN-based as a negative electrode rather than the conventional capacitive carbon-based electrodes rendered some advantages, where it has higher capacity, and it resembles the supercapacitance and OPW of the positive electrode materials leading to an ASC with higher energy density.

According to the investigation of Liu et al. [41] and Sun et al. [42], the electrodes were binder-free. The electroactive materials were directly synthesized on the CC substrates to avoid using polymer binders that limit the permeation of the electrolyte to the inner electrode and the transfer of electrons in the electrode [41]. Although Yun-Peng et al. [43] produced MOF in powder form and then transferred it onto CC using a polymer binder (PVDF), they eliminated the negative effects of using a binder by adopting other enhancement techniques for the overall performance of the electrode. One of these techniques used to improve the conductivity was the electrodeposition of the conductive polymer polypyrrole (PPy). Figure 2a shows a comparison between the CV of the $\text{Cu}_9\text{S}_8\text{-CC}$, $\text{Cu}_9\text{S}_8\text{@C-CC}$, and $\text{PPy/Cu}_9\text{S}_8\text{@C-CC}$ electrodes. It is evident that the capacitance of the $\text{PPy/Cu}_9\text{S}_8\text{@C-CC}$ is the highest, where it renders the biggest area under the CV curve. The $\text{PPy/Cu}_9\text{S}_8\text{@C-CC}$ electrode was further tested under different scan rates and retained the original shape, as shown in Figure 2b, indicating a good rate performance. Additionally, in the GCD curves presented in Figure 2c the $\text{PPy/Cu}_9\text{S}_8\text{@C-CC}$ electrode had the longest charge/discharge time. Figure 2d shows the GCD curves of the electrode obtained at different current densities. The good capacitive performance of the $\text{PPy/Cu}_9\text{S}_8\text{@C-CC}$ electrode was also observed in its EIS result of a straight line that is nearly parallel to the imaginary axis (Figure 2e). The very good electrochemical performance of the electrode was also noticed in the good cyclic stability of 80.36% (3000 cycles), as shown in Figure 2f.

Carbon cloths render limited surface area. To address this issue, Ying et al. [44] introduced carbon nanowall arrays (CNWAs) as a secondary substrate to increase the mass loading of the electroactive materials. The authors synthesized a MOF-based electrode as a cathode in ASCs, where CNWAs were constructed on carbon cloth and then manipulated with a thin layer of Ni. The latter worked as a crosslinking layer between the secondary substrate CNWAs and the nickel-cobalt sulfide nanosheets to obtain $\text{CC/CNWAs@Ni@Co-Ni}_2\text{S}_4$ electrode. Figure 3 shows a schematic illustration of the synthesis procedure for the hierarchical electrode. Adding the Ni layer enhanced the ion/electron diffusion rate and significantly decreased the interfacial resistance between CNWAs and CoNi_2S_4 , hence creating electronic “superhighways” for fast charge storage and transfer. The electrode exhibited a high specific capacitance of 3163 F g^{-1} at 1 A g^{-1} , very good rate capability, and outstanding electrochemical stability with 95.5% capacity retention after 10,000 cycles. A hybrid ASC was fabricated with $\text{CC/CNWAs@Ni@Co-Ni}_2\text{S}_4$ as a positive electrode and commercial AC as a negative electrode. The device rendered excellent specific capacitance (151.3 F g^{-1} at 1 A g^{-1}), high energy and power densities (53.8 Wh kg^{-1} and 801 W kg^{-1} , respectively), and high cycling stability with 90.1% capacity retention after 10,000 cycles.

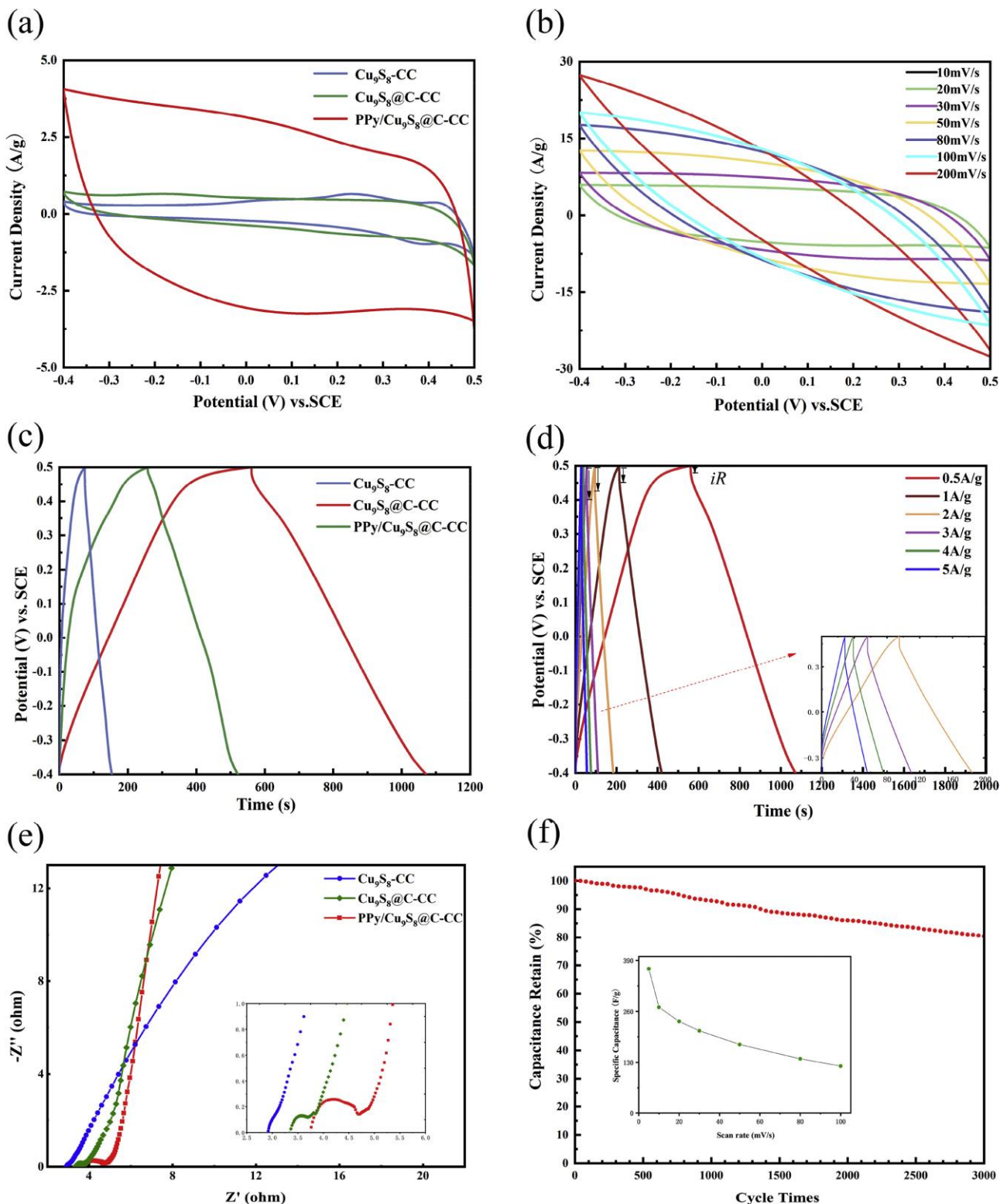


Figure 2. (a) CV behaviors of $\text{Cu}_9\text{S}_8\text{-CC}$, $\text{Cu}_9\text{S}_8\text{@C-CC}$, and $\text{PPy/Cu}_9\text{S}_8\text{@C-CC}$ electrode. (b) CV curves of $\text{PPy/Cu}_9\text{S}_8\text{@C-CC}$ electrode at different scan rates. (c) GCD curves of $\text{Cu}_9\text{S}_8\text{-CC}$, $\text{Cu}_9\text{S}_8\text{@C-CC}$, and $\text{PPy/Cu}_9\text{S}_8\text{@C-CC}$ electrode. (d) GCD curves of $\text{PPy/Cu}_9\text{S}_8\text{@C-CC}$ electrode at different current densities. (e) Nyquist electrochemical impedance spectra of $\text{Cu}_9\text{S}_8\text{-CC}$, $\text{Cu}_9\text{S}_8\text{@C-CC}$, and $\text{PPy/Cu}_9\text{S}_8\text{@C-CC}$ electrode. (f) Cycling stability of $\text{PPy/Cu}_9\text{S}_8\text{@C-CC}$ electrode at 10 mV/s, the insert is variation of specific capacitance at different scan rates [43]. Copyright 2019 Elsevier.

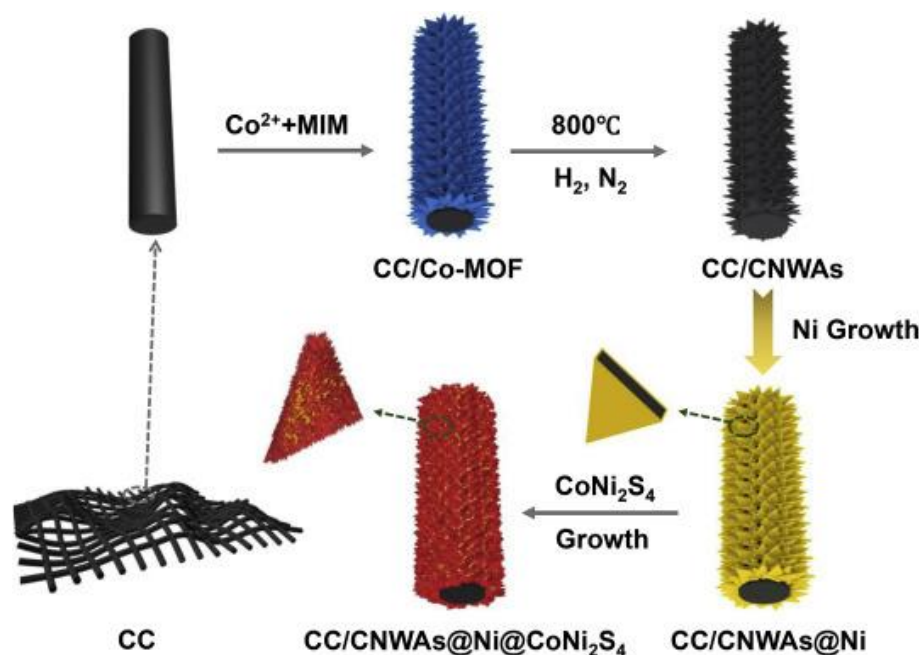


Figure 3. Schematic illustration of synthesis procedure for the hierarchical CC/CNWAs@Ni@CoNi₂S₄ nanosheet arrays electrode [44]. Copyright 2019 Elsevier.

Compared with the CC substrate, the 3D porous metal foams such as Ni foam exhibit a much higher surface area, and therefore the loading extent of the active material is greater. Ahmed et al. [45] synthesized MOF-derived hierarchical copper-cobalt sulfide nanosheet (CuCo₂S₄ NS) arrays on Ni foam substrate as a pseudocapacitive electrode for ASCs. The electrode possessed enriched electroactive sites and short ion/electron diffusion pathways. The CuCo₂S₄ NS electrode manifested excellent electrochemical performance with an ultra-high specific capacity, exceptional rate capability, and ascendant cycling stability. An ASC device was synthesized using the CuCo₂S₄ NS as a positive electrode and iron oxide anchored nitrogen-doped graphene (Fe₂O₃/NG) aerogel as a negative electrode. The solid-state device accomplished high energy and power densities, high volumetric capacity, and ultra-long cycle life with values of $\sim 89.6 \text{ W h kg}^{-1}$, $\sim 663 \text{ W kg}^{-1}$, $\sim 2.1 \text{ mA h cm}^{-3}$ at a current density of 3 mA cm^{-2} , and $\sim 91.5\%$ capacity retention after 10,000 cycles, respectively. The authors also reported that the MOFs prepared with urea as a linker manifested poorly interconnected nanosheet arrays with lower porosity than those with 2-methylimidazole as a linker.

One of the reasons that limit the production of aqueous supercapacitors is their low durability. For instance, MOFs are porous structures, but the majority of them are chemically not stable when in contact with aqueous electrolytes and hence lose their hierarchical structure leading to degradation in their performance. To overcome such an issue, Weibin et al. [46] developed a new MOF-based positive electrode for aqueous supercapacitors. The electrode comprises cobalt ZIF-67 hierarchical hollow nanocages coated with carbon from resorcinol-formaldehyde (ZIF-67@RF); these nanocages were further treated via sulfidation (where thioacetamide (TAA) was used as a sulfurizing agent) followed by annealing to obtain CoS_x/C, then the structure was transferred to a carbon layer. The aim of RF coating was to enhance the hollow structure's stability and improve the charge transfer process. According to the authors, the CoS_x/C hierarchical hollow nanocages with the optimum carbon coating (optimum RF extent) exhibited good specific capacitance, outstanding rate performance (83.6% capacitance retention), and excellent cycling stability even after 10,000 cycles.

Another advantage of coating the nanostructures with carbon is to reduce the charge transfer resistance in the electrode. Wei et al. [47] adopted this technique by preparing carbon-coated spherical sulfide nanoparticles by simultaneous carbonization and sulfuriza-

tion using MOFs as the precursors. The authors developed monometal-based MOF NiS@C and bimetal-based MOF (NiCo₂S₄@C). The carbonization and sulfurization endowed the electrodes with high electrochemical activity and significantly improved conductivity. Moreover, the obtained bimetallic precursor exhibited more electrochemical active sites, therefore, resulting in better electrochemical performance than the monometallic MOF precursor. NiCo₂S₄@C manifested a high specific capacity of 948.9 C g⁻¹ at 1 A g⁻¹ compared to 631.0 C g⁻¹ for the NiS@C, which is demonstrated in Figure 4, which shows the CV and GCD of the monometal-based and bimetal-based electrodes with additional electrochemical results for the NiCo₂S₄@C electrode. The NiCo₂S₄@C electrode rendered the biggest area under the CV curve and the longest charge/discharge time when comparing its GCD curve with those of the other electrodes. A hybrid ASC was assembled with NiCo₂S₄@C as the positive electrode and AC as the negative electrode. The device's energy density was calculated to be 43.8 Wh kg⁻¹ with a power density of 799.1 W kg⁻¹, and the capacitance retention rate was 81.9% after 5000 cycles.

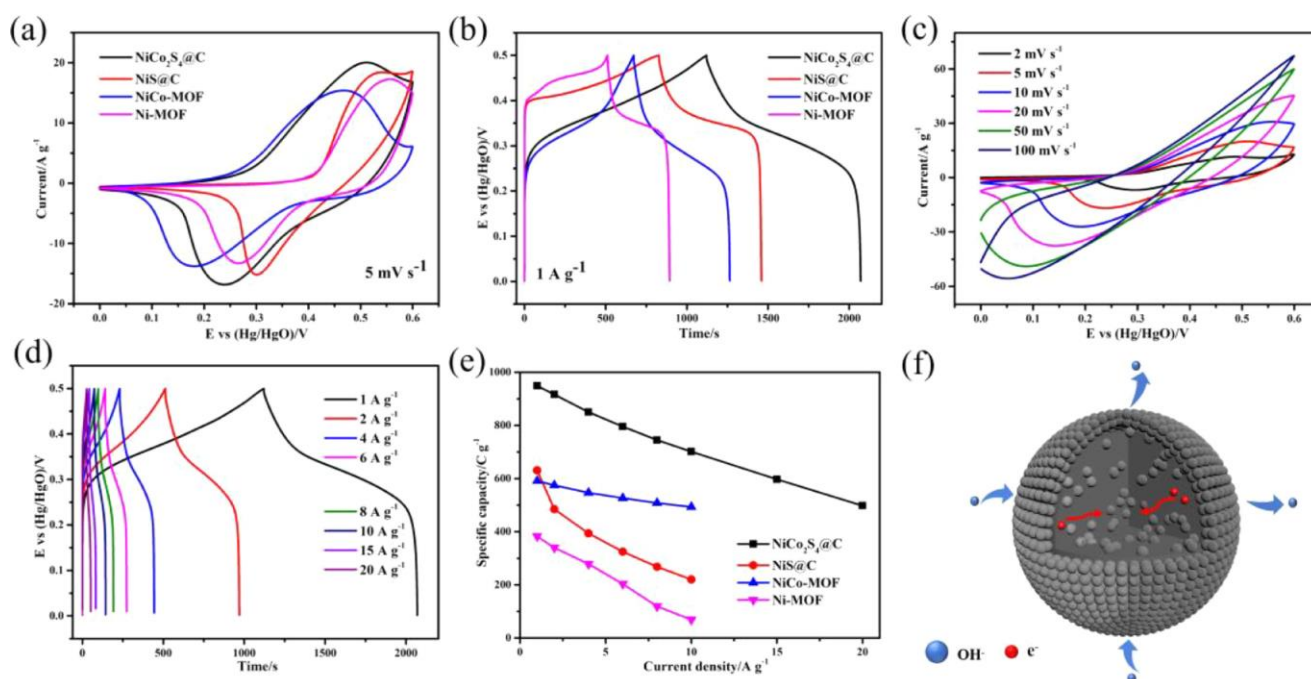


Figure 4. (a) CV and (b) GCD curves of NiCo₂S₄@C, NiS@C, NiCo-MOF, and Ni-MOF electrodes at a scan rate of 5 mV s⁻¹ and a current density of 1 A g⁻¹, respectively. (c) CV curves of NiCo₂S₄@C electrode at scan rates from 2 to 100 mV s⁻¹, (d) GCD curves of NiCo₂S₄@C electrode at current densities from 1 to 20 A g⁻¹. (e) Specific capacity of NiCo₂S₄@C, NiS@C, NiCo-MOF and Ni-MOF electrodes measured at different current densities. (f) Schematic illustration of the sulfide microsphere composed of carbon-coated nanoparticles [47]. Copyright 2021 Elsevier.

To improve the sluggish ion/electron transport kinetics in the metal sulfide-based electrodes, conductive reduced graphene oxide (rGO) was proposed to be utilized as a substrate. Peng et al. [48] synthesized a composite of hollow Co₉S₈ (ZIF-67 as an electrode for supercapacitors, which was sulfurized using a TAA agent) on rGO. The rGO/Co₉S₈ showed high specific capacitance, improved high-rate capability, and good cycling stability.

Co-based and NiCo-based MOFs gained a special interest in energy storage applications since Co and Ni are earth-abundant elements. Dongxuan et al. [49] prepared NiCo₂S₄ and CoS₂ nanoarrays with a hollow/porous configuration derived from pentagon-like ZIF-67 on Ni foam for asymmetrical supercapacitors. The hollow/porous structure of the electrodes' materials revealed improved electroactive sites, shortened charge/ion diffusion length, and enhanced mass/electron transfer. According to the authors, the ASC associated

with NiCo_2S_4 and CoS_2 as cathode and anode, respectively, resulted in a high energy density of 55.8 Wh/kg with a power density of 695.2 W/kg.

Implementing core-shell nanostructured composites endows the electrodes of SCs with several features, such as larger surface area, more reactive sites, and the enlarged contact area between the electrochemically active components and the void space, which reduce the volume change during the discharging/charging cycles. These features enhance the electrochemical performance of the electrodes and furnish the devices with higher energy and power densities. Xiaocheng et al. [50] exploited these features by preparing core-shell structured nanocubes composites consisting of MoS_2 , Co_9S_8 , and doped carbon interlayer ($\text{Co}_9\text{S}_8@\text{N}-\text{C}@\text{MoS}_2$). The electrode was synthesized using ZIF-67 as a precursor via hydrothermal reaction, calcination, and vulcanization process. The electrode with the mass ratio of 1:2 between the $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CH}_4\text{N}_2\text{S}$ (thiourea; sulfurizing agent) showed the best performance with a specific capacitance of 410.0 F g^{-1} at 10.0 A g^{-1} and 101.7% capacitance retention after 20,000 cycles. The retention of capacitance values that are greater than the initial value was attributed to the probable activation of materials in the cycling process [51].

It is expected that trimetallic sulfides would exhibit enhanced synergistic effects, more mixed-valence states, and richer redox-active centers than their corresponding single and bimetallic sulfides. Chenxia et al. [52] synthesized MOF-derived hollow rod-like NiCoMn ternary metal sulfides nanosheets. The procedure for the preparation method of this ternary metal-metal material is shown schematically in Figure 5. In brief, the hydrothermal method was used to synthesize ZIF-67, which is then used as a template and cobalt source, along with $\text{Ni}(\text{NO}_3)_2$ as a nickel source, and MnCl_2 as a manganese source to prepare NiCoMn-OH nanosheets through the hydrolysis-controlled ion exchange reaction. The final NiCoMn-S material was obtained by converting the NiCoMn-OH nanosheets via the hydrothermal method with TAA as the sulfurization agent. The NiCoMn-S electrode with the optimum weight ratio between the Ni, Co, and Mn metals' ions exhibited the best morphology and electrochemical performance. The authors prepared different electrodes for the purpose of comparisons, namely, single metal sulfide, bimetallic sulfides, and ternary metal sulfides with different weight ratios. These electrodes are Co-S, NiCo-S, CoMnS, $\text{Ni}_1\text{CoMn}_3\text{-S}$, $\text{Ni}_3\text{CoMn}_1\text{-S}$, and NiCoMn-S (all prepared on Ni foam substrates); among these electrodes, the NiCoMn-S electrode showed the best performance. It was attributed that trimetal sulfides can afford stronger synergy than monometal or bimetal sulfides, and the optimal ratio between the transition metals (Ni, Co, and Mn) can afford the maximum synergy between these metals. Tables 1 and 2 summarize the characteristic values of the sulfurized MOF-based electrodes and the parameters of the synthesized SCs, respectively.

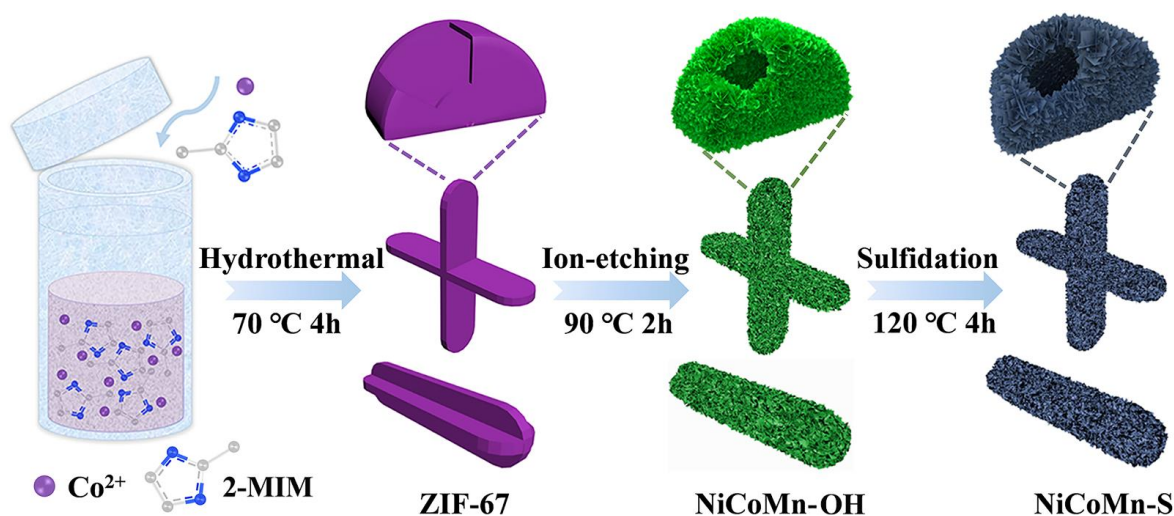


Figure 5. The preparation process of hollow rod-like NiCoMn-S ternary metal sulfide [52]. Copyright 2022 Elsevier.

Table 1. Summary of the electrochemical parameters of the sulfurized MOF-based electrodes in three-electrode measurement systems for supercapacitor application.

No.	Electrode	Sulfurization Method	Electrolyte	Capacitance/Capacity	Scan Rate/Current Density	Potential Window	Cyclic Stability	Specific Surface Area	Ref
1	NiCoS/CC	Ion exchange process	2 M KOH	1653 F g ⁻¹	1 A g ⁻¹	0–0.6 V	84% (3000 cycles)	-	[41]
2	NiCo ₂ S ₄	Ion exchange process (TAA as sulfurizing agent)	6 M KOH	939 C g ⁻¹	1 A g ⁻¹	From −0.1 to 0.6 V	92.8% (5000 cycles)	79.3 m ² g ⁻¹	[49]
3	CoS ₂ (Anode)	Ion exchange process (TAA as sulfurizing agent) followed by annealing in N ₂ at 350 °C	6 M KOH	343.5 C g ⁻¹	1 A g ⁻¹	From −1 to 0 V	-	-	[49]
4	Ni(OH) ₂ @ZnCoS-NSs	Hydrothermal anion-exchange reaction	2 M KOH	2730 F g ⁻¹ (8.1 F cm ⁻²)	3 mA cm ⁻²	From 0 to 0.45 V	87% (10,000 cycles)	-	[42]
5	VN@ZnCoS-NS (Anode)	Hydrothermal anion-exchange reaction	2 M KOH	1.35 F cm ⁻²	3 mA cm ⁻²	From −1.2 to −0.2 V	80% (10,000 cycles)	-	[42]
6	CC/CNWAs@Ni@Co-Ni ₂ S ₄	Electrochemical co-deposition	1 M KOH	3163 F g ⁻¹	1 A g ⁻¹	From −0.2 to 0.6 V	93.0% (10,000 cycles)	-	[44]
7	CC@CoO@S-Co ₃ O ₄	Hydrothermal reaction with thioacetamide	2 M KOH	1013 mF cm ⁻²	1 mA cm ⁻²	From 0 to 0.5 V	~67.7% (5000 cycles)	24.7 m ² g ⁻¹	[53]
8	CuCo ₂ S ₄ NS	Ion-exchange process.	2 M KOH	~409.2 mA h g ⁻¹	3 mA cm ⁻²	From −0.2 to 0.7 V	~94.2% (10,000 cycles)	~132.92 m ² g ⁻¹	[45]
9	CoS _x /C-2	Solvothermal method	1 M KOH	618.4 F g ⁻¹	2 A g ⁻¹	From 0 to 0.5 V	ca. 100% (10,000 cycles)	-	[46]
10	Cu ₇ S ₄ /C	Calcining-hydrothermal process	1 M H ₂ SO ₄	229.6 F g ⁻¹ (57.4 mAh g ⁻¹)	1 A g ⁻¹	From −0.2 to 0.7 V	78.1% (3000 cycles)	-	[54]
11	NiCo ₂ S ₄ @C	Simultaneous carbonization and sulfurization of the MOF in the presence of sulfur source under inert atmosphere at relatively high temperatures	1 M KOH	948.9 C g ⁻¹	1 A g ⁻¹	From 0 to 0.6 V	71.4% (3000 cycles)	-	[47]
12	PPy/Cu ₉ S ₈ @C-CC	Calcination–vulcanization method	1M KCL	270.72 F g ⁻¹	10 mV/s	From −0.4 to 0.5 V	80.36% (3000 cycles)	-	[43]
13	rGO/Co ₉ S ₈	Hydrothermal method	1 M KOH	575.9 F g ⁻¹	2 A g ⁻¹	From 0 to 0.45 V	92.0% (9000 cycles)	-	[48]
14	Ni _x S _y @CoS	Obtained by adding TAA at mild room temperature without further thermal-treatment	6 M KOH	2291 F g ⁻¹	1 A g ⁻¹	From −0.1 to 0.25 V	85.2% (2000 cycles)	180.7 m ² g ⁻¹	[55]
15	Co ₉ S ₈ @N–C@MoS ₂	Hydrothermal method	3 M KOH	410.0 F g ⁻¹	10 A g ⁻¹	From 0 to 0.6 V	101.7% (20,000 cycles)	-	[50]
16	NiCoMn-S	Hydrothermal method	1 M KOH	2098.2 F g ⁻¹	1 A g ⁻¹	From 0 to 0.7 V	71.6% (4000 cycles)	94.9 m ² g ⁻¹	[52]

Table 2. Summary of the electrochemical parameters of the sulfurized MOF-based electrodes in two-electrode measurements (Device).

No.	Positive Electrode Material	Negative Electrode Material	Electrolyte	Capacitance/Capacity	Scan Rate/Current Density	Potential Window	Energy Density	Power Density	Cyclic Stability	Ref
1	NiCoS/CC	Activated carbon	2 M KOH	128 F g ⁻¹	0.5 A g ⁻¹	From 0 to 1.5 V	40 Wh kg ⁻¹	379 W kg ⁻¹	84% (7000 cycles)	[41]
2	NiCo ₂ S ₄	CoS ₂	2 M KOH	287 C g ⁻¹	1 A g ⁻¹	From 0 to 1.4 V	55.8 Wh kg ⁻¹	695.2 W kg ⁻¹	91.9% (5000 cycles)	[49]
3	Ni(OH) ₂ @ZnCoS-NSs	VN@ZnCoS-NS	PVA/KOH	210.7 F g ⁻¹	0.5 A g ⁻¹	From 0 to 1.6 V	75 W h kg ⁻¹	0.4 kW kg ⁻¹	82% (10,000 cycles)	[42]
4	CC/CNWAs@Ni@Co-Ni ₂ S ₄	Activated carbon	1 M KOH	151.3 F g ⁻¹	1 A g ⁻¹	From 0 to 1.6 V	53.8 Wh kg ⁻¹	801 W kg ⁻¹	90.1% (10,000 cycles)	[44]
5	CC@CoO@S-Co ₃ O ₄	MOF-derived carbon	PVA/KOH	1.99 F cm ⁻³	2 mA cm ⁻²	From 0 to 1.5 V	0.71 mW h cm ⁻³	21.3 mW cm ⁻³	87.9% (5000 cycles)	[53]
6	CuCo ₂ S ₄ NS	Fe ₂ O ₃ /NG	PVA/KOH	~2.1 mA h cm ⁻³	3 mA cm ⁻²	From 0 to 1.6 V	~89.6 Wh kg ⁻¹	~663 W kg ⁻¹	~91.5% (10,000 cycles)	[45]
7	NiCo ₂ S ₄ @C	Activated carbon	1 M KOH	123.3 F g ⁻¹	1 A g ⁻¹	From 0 to 1.6 V	43.8 Wh kg ⁻¹	799.1 W kg ⁻¹	81.9% (5000 cycles)	[47]
8	NiCoMn-S	Activated carbon	1 M KOH	124.5 F g ⁻¹	1 A g ⁻¹	From 0 to 1.7 V	50.0 Wh kg ⁻¹	850.0 W kg ⁻¹	73.6% (6000 cycles)	[52]

3. Metal Selenides in Supercapacitors

Metal selenides exhibit higher conductivity, lower electronegativity, faster reaction kinetics, and higher volume-specific capacity than their sulfide counterparts [56,57]. These characteristics make metal selenides attractive candidates in the field of supercapacitors. Table 3 summarizes the performance of the selenization-treated MOF-based electrodes, and the performance of their corresponding devices is listed in Table 4.

In addition to cobalt sulfides, cobalt selenides are also commonly studied for hybrid SCs [58–63] due to their diverse structures, theoretically high capacity, suitable operating voltage window, and excellent electrical conductivity compared with cobalt oxides [64–66]. Since bimetallic MOFs-based electrodes revealed better electrochemical performance than the single metallic MOFs, Peiheng et al. [67] prepared (CuCo)Se nanoparticles embedded in N-doped carbon layers through the selenization treatment (under an inert atmosphere and high temperature) of bimetallic MOF CuCo-ZIF. By comparing the SEM image of the (CuCo)Se/NC-0.5 in Figure 6B and its precursor in Figure 6A, it can be seen that after the selenization process, the original polyhedral structures were almost retained with a rough surface. SEM and TEM images of (CuCo)Se/NC-0.5, which have the optimum loading of Cu precursor, are shown in Figure 6. The (CuCo)Se/NC-0.5 electrode, which has the optimum loading of Cu precursor, rendered promoted electrochemical performance in terms of specific capacity, rate capability, and cycling stability. The hybrid ASC device (CuCo)Se/NC-0.5//AC manifested good energy density cycling stability over 5000 cycles (Figure 7).

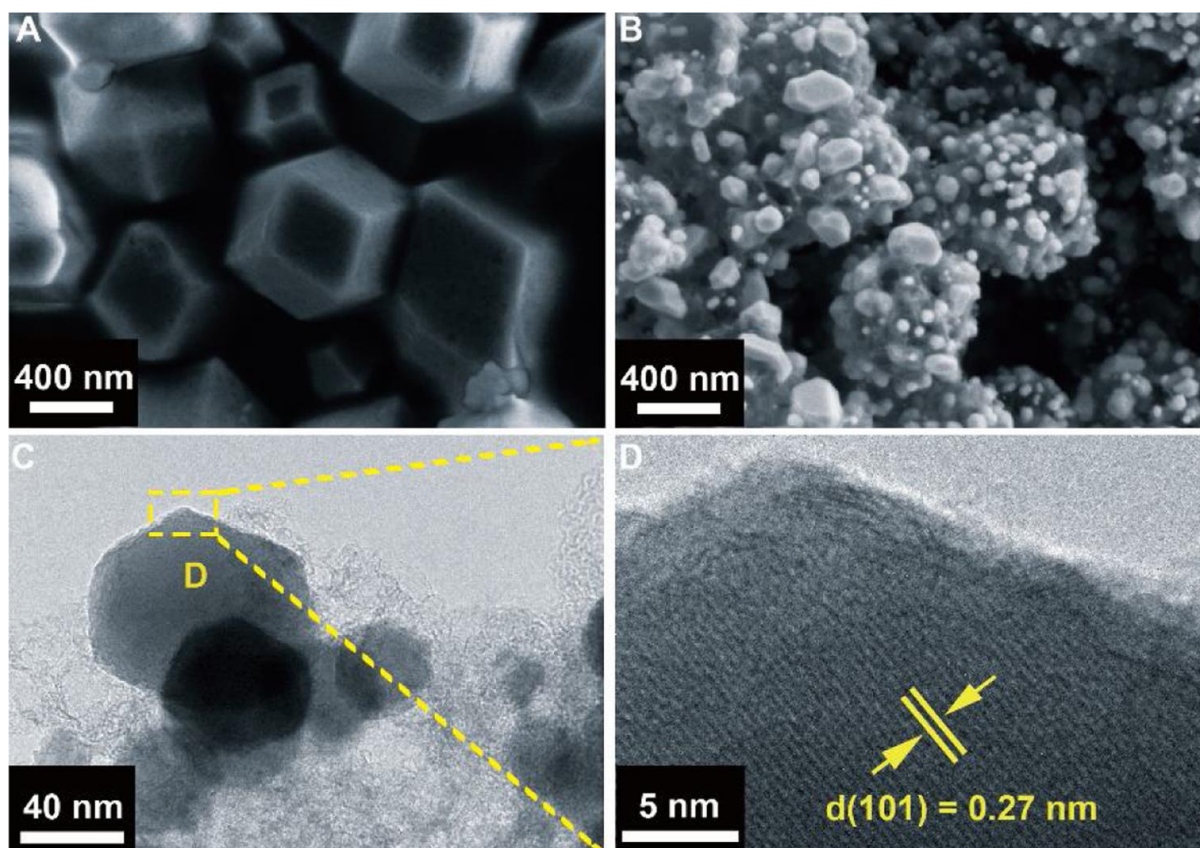


Figure 6. (A) SEM image of CuCo-ZIF-0.5, (B) SEM image of (CuCo)Se/C-0.5, (C) TEM and (D) HRTEM images of (CuCo)Se/C-0.5, respectively [67]. Copyright 2021 Elsevier.

Similarly, Liang et al. [68] synthesized hierarchical $(\text{Ni}_{0.33}\text{Co}_{0.67})\text{Se}_2$ complex hollow spheres (CHSs) with a hierarchical porous surface. The fabrication process involves annealing for transforming the solid spheres of Ni-Co-MOF onto NiCo_2O_4 multi-shelled

hollow spheres (MHSs) templates, which are then converted onto $(\text{Ni}_{0.33}\text{Co}_{0.67})\text{Se}_2$ CHSs through a hydrothermal selenization method. The $(\text{Ni}_{0.33}\text{Co}_{0.67})\text{Se}_2$ demonstrated remarkably improved electrochemical performance compared with the NiCo_2O_4 MHSs precursor. According to the authors, an ASC device employing $(\text{Ni}_{0.33}\text{Co}_{0.67})\text{Se}_2$ as the positive electrode and AC as the negative electrode exhibited a high energy density of 29.1 Wh kg^{-1} at a power density of 800 W kg^{-1} .

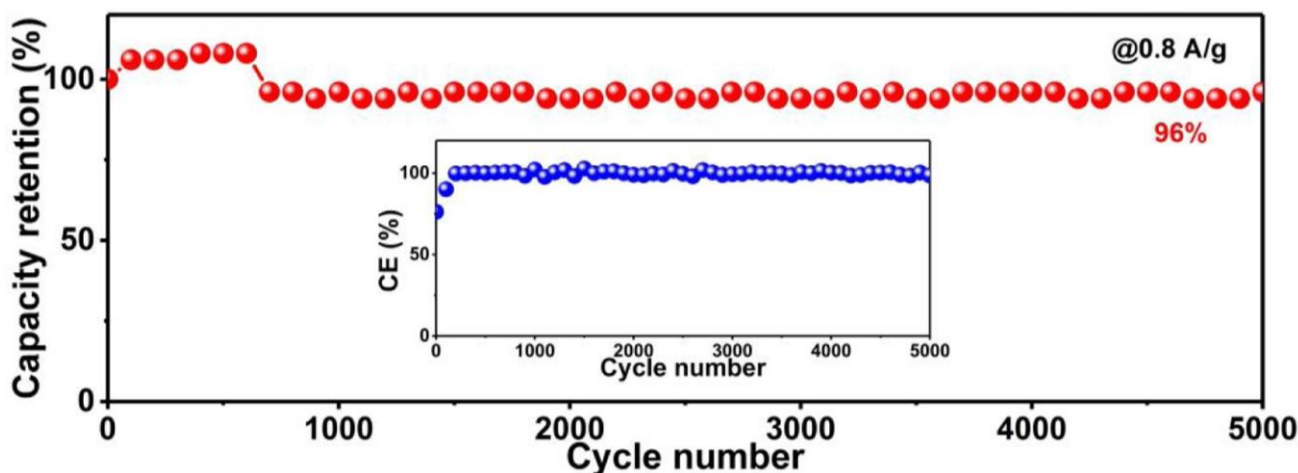


Figure 7. Cycling performance of the HSC device tested at 0.8 A/g over 5000 cycles. Red balls represent capacity retention, while the blue balls in the inset represent Coulombic efficiency [67]. Copyright 2021 Elsevier.

It is worth mentioning that although bimetallic MOFs may have a smaller specific surface area (SSA) and smaller pore sizes than single-metal MOFs, the electrochemical performance of the bimetallic MOFs is still better than that of the single-metal MOFs. To demonstrate this, Chenxu et al. [69] compared the single metallic cobalt selenide MOF (CoSe_2) and the bimetallic hollow cobalt molybdenum selenide (Co-Mo-Se) nanosheet arrays. The authors calculated the SSA and the peak pore diameter of the CoSe_2 and found them to be $72.9 \text{ m}^2 \text{ g}^{-1}$ and 3.9 nm , respectively, which are larger than those for the Co-Mo-Se ($64.5 \text{ m}^2 \text{ g}^{-1}$ and 3.5 nm). On the other hand, the bimetallic Co-Mo-Se electrode manifested better charge storage performance with a specific capacity of 221.7 mAh g^{-1} , which is significantly higher than 146.7 mAh g^{-1} for the CoSe_2 electrode. This could be attributed to the fact that the bimetallic selenides possess more Faradaic reaction sites and abundant structural deficiencies due to the coexistence of various metal ions and synergistic effects [70,71]. The durability of the Co-Mo-Se electrode was better than that of the CoSe_2 electrode. This likely arose from the distinctive hollow nanosheet structure that is capable of providing sufficient inner spaces to afford the swelling stress acquired from the volume expansion. In addition to bimetallic selenide MOF-based electrodes, researchers investigated trimetal nanostructures for SC electrodes [72,73]. These electrodes demonstrated outstanding electrochemical performance.

Electrochemical properties and cycle stability of the electrode materials could be enhanced by ionic doping. The introduction of transition metal ions helps control the electron densities based on the defects generated by doped heteroatoms and realigning valence electrons, which expedite electron transfer, leading to advanced catalytic and electrochemical performance. One of these transition metal ions is Mo^{6+} , which has high positive valence and a small ionic radius. Accordingly, Yulu et al. [74] fabricated Mo-doped LDHs@MOF-Se, a core-shell structured triangle-like array on CC substrate as a battery-type electrode. First, Zn-Co-based MOF selenide (MOF-Se) arrays were synthesized as the core via hydrothermal method followed by selenization treatment in a Se medium and then covered by Mo-doped NiCo-LDH nanoflakes (Mo-doped LDHs) using electrodeposition method. The advantage of Mo-doping is to obtain LDHs with high redox activity and

facilitate ion movement along the inter-sheet planes when the precursors hydrolyze, which enhances the faradaic charge storage [75,76]. The Mo-doped LDHs@MOF-Se hierarchical electrode showed a defect-rich electronic state, large active area, and rich reaction sites, which endowed high areal capacity and high rate capability [74]. To demonstrate the integrity of this electrode material in SCs application, an asymmetric device was fabricated using Mo-doped LDHs@MOF-Se as a positive electrode and AC as a negative electrode. The ASC exhibited high energy density and an ultralong lifespan of 94% maintenance of the original capacitance after 10,000 cycles of GCD.

Metal phosphides possess more metalloid characteristics due to the presence of multi-electron orbitals, and they exhibit better conductive properties and higher capacity than metal oxides and hydroxides [77]. Kisan et al. [78] demonstrated the advantages of metal phosphides and metal selenides by preparing selenium-infiltrated cobalt phosphide nanostructure arrays (CPNA) from a 2D Co-MOF precursor through successive phosphidization and selenium infiltration processes. The materials were synthesized on activated carbon fiber textile (ACFT) substrate to obtain the $\text{Se}_x\text{@CPNA-ACFT}$ electrode for flexible quasi-solid-state ASCs. Under the three-electrode measurements, the results showed the best electrochemical performance was obtained by the electrode with the optimum amount of Se; $\text{Se}_{0.6}\text{@CPNA-ACFT}$. This was attributed to the high porosity that provided additional active sites and to the strong interaction between Se and CPNA, which prohibits the dissolution of Se in the electrolyte. The CV results revealed that the electrode possesses both diffusion-controlled and surface capacitive charge storage mechanisms, signifying the pseudocapacitive behavior of the electrode materials. The $\text{Se}_x\text{@CPNA-ACFT}$ electrode was selected to be the positive electrode of an ASC with FeS_2 decorated rGO at etched CFT ($\text{FeS}_2\text{@rGO-ECFT}$) as a negative electrode. According to the authors [40], the device revealed an outstanding performance with a high specific energy density of $\sim 70.6 \text{ Wh kg}^{-1}$ at a power density of 335 W kg^{-1} .

To summarize, Figure 8 shows the Ragone plot for some of the mentioned articles in this review. It can be seen that the ASCs, which consist of two different pseudocapacitive electrodes (such as $\text{CuCo}_2\text{S}_4 \text{ NS//Fe}_2\text{O}_3\text{/NG}$ [45], $\text{Ni(OH)}_2\text{@ZnCoS-NSs//VN@ZnCoS-NS}$ [42], and $\text{Se}_{0.6}\text{@CPNA-ACFT//FeS}_2\text{@rGO-ECFT}$ [78]), possess the highest specific energy densities. On the other hand, hybrid ASCs with activated carbon as an anode exhibited lower specific energy densities but higher specific power densities. The ASC MnSe@NF//AC [72] manifested a synergetic behavior with high energy and power densities.

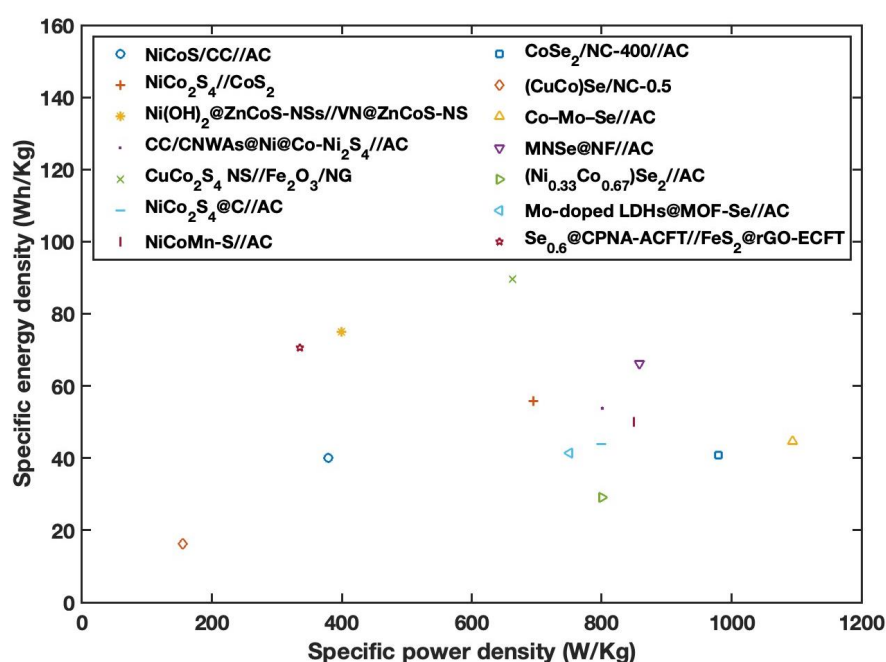


Figure 8. Ragone plot for the supercapacitors [14,15,17,18,20,22,24,31–33,36,38,40,41].

Table 3. Summary of the electrochemical parameters of the selenization-treated MOF-based electrodes in three-electrode measurement systems for supercapacitor application.

No.	Electrode	Selenization Method	Electrolyte	Capacitance/Capacity	Scan Rate/Current Density	Potential Window	Cyclic Stability	Specific Surface Area	Ref
1	CoSe ₂ /NC-400	Annealing at high temperature in the presence of Se powder	6 M KOH	120.2 mA h g ⁻¹	1 A g ⁻¹	From 0 to 0.4 V	92% (10,000 cycles)	74.6 m ² g ⁻¹	[79]
2	CoSe ₂ /CNT	Hydrothermal method	3 M KOH	-	-	From -0.2 to 0.3 V	-	58.3 m ² g ⁻¹	[58]
3	(CuCo)Se/NC-0.5	Direct selenization in the presence of Se powder under inert atmosphere at high temperature	2 M KOH	121.4 C g ⁻¹	1 A g ⁻¹	From -0.1 to 0.6 V	130% (1200 cycles)	-	[67]
4	Co-Mo-Se	Hydrothermal process	6 M KOH	221.7 mAh g ⁻¹	1 A g ⁻¹	From 0 to 0.6 V	95% (8000 cycles)	64.5 m ² g ⁻¹	[69]
5	MNSe@NF	Hydrothermal method	6 M KOH	325.6 mA h g ⁻¹ (1172.16 C g ⁻¹)	2 A g ⁻¹	From 0 to 0.7 V	96.8% (15,000 cycles)	~101.8 m ² g ⁻¹	[72]
6	(Ni _{0.33} Co _{0.67})Se ₂	Hydrothermal selenization method	3 M KOH	827.9 F g ⁻¹	1 A g ⁻¹	From 0 to 0.6 V	Calculated 113.6% (2000 cycles)	23.82 m ² g ⁻¹	[68]
7	H-Ni-Co-Se	Hydrothermal selenization	-	175 F g ⁻¹	1 A g ⁻¹	From -0.2 to 0.6 V	89.3% (2000 cycles)	20.77 m ² g ⁻¹	[57]
8	Zn-Ni-Se/Ni(OH) ₂	Hydrothermal selenization	6 M KOH	1632.8 F g ⁻¹	2 A g ⁻¹	From 0 to 0.6 V	85.4% (2000 cycles)	-	[73]
9	Mo-doped LDHs@MOF-Se	Selenization treatment of the MOF arrays in a Se atmosphere	KOH	5.16 C cm ⁻²	2 mA cm ⁻²	From 0 to 0.6 V	81.4% (3000 cycles)	-	[74]
10	Se _{0.6} @CPNA-ACFT	Selenium infiltration (at high temperature in the presence of Se powder.	3 M KOH	302 mAh g ⁻¹ (~0.602 mAh cm ⁻²)	1 mA cm ⁻²	From -0.1 to 0.6 V	~93.8% (10,000 cycles)	51.7 m ² g ⁻¹	[78]

Table 4. Summary of the electrochemical parameters of the selenization-treated MOF-based electrodes in two-electrode measurements (Device).

No.	Positive Electrode Material	Negative Electrode Material	Electrolyte	Capacitance/Capacity	Scan Rate/Current Density	Potential Window	Energy Density	Power Density	Cyclic Stability	Ref
1	CoSe ₂ /NC-400	Activated carbon	6 M KOH	58.4 mA h g ⁻¹	1 A g ⁻¹	From 0 to 1.4 V	40.9 Wh kg ⁻¹	980 W kg	90.2% (10,000 cycles)	[79]
2	CoSe ₂ /CNT	FeSe ₂ /CNT	-	-	-	From 0 to 1.8 V	0.25 mWh cm ⁻²	53.06 mW cm ⁻²	~85.29% (4000 cycles)	[58]
3	(CuCo)Se/NC-0.5	Activated carbon	-	-	-	From 0 to 1.6 V	~16.3 Wh kg ⁻¹	155.3 W kg ⁻¹	96% (5000 cycles)	[67]
4	Co-Mo-Se	Activated carbon	KOH/PVP	57.7 mAh g ⁻¹	-	From 0 to 1.6 V	44.7 Wh kg ⁻¹	1094 W kg ⁻¹	90.7% (8000 cycles)	[69]
5	MNSe@NF	Activated carbon	cellulose paper/6 M KOH	62.4 mA h g ⁻¹ 224.65 C g ⁻¹	1 A g ⁻¹	From 0 to 1.7 V	66.1 Wh kg ⁻¹	858.45 W kg ⁻¹	94.1% (15,000 cycles)	[72]
6	(Ni _{0.33} Co _{0.67})Se ₂	Active carbon	-	81.9 F g ⁻¹	1 A g ⁻¹	From 0 to 1.6 V	29.1 Wh kg ⁻¹	800 W kg ⁻¹	-	[68]
7	Mo-doped LDHs@MOF-Se	Activated carbon	KOH	132.0 F g ⁻¹	1 A g ⁻¹	From 0 to 1.5 V	41.3 Wh kg ⁻¹	750.0 W kg ⁻¹	94% (10,000 cycles)	[74]
8	Se _{0.6} @CPNA-ACFT	FeS ₂ @rGO-ECFT	PVA/KOH	~88 mAh g ⁻¹ ~1.81 mAh cm ⁻³	2 mA cm ⁻²	From 0 to 1.6 V	~70.6 Wh kg ⁻¹	335 W kg ⁻¹	92.4% (10,000 cycles)	[78]

4. Sulfur-Doped MOF-Derived Catalysts for Fuel Cells Application

In addition to its outstanding performance as electrode materials in supercapacitors, MOF-derived transition metal sulfides rendered excellent performance when used as catalysts in Fuel cells. The significance of doping the catalyst with S atoms rather than P or B atoms is that the relatively large size of sulfur atoms creates defects and porous structure that leads to a high surface area, accelerated electron transfer, and oxygen adsorption, hence enhanced ORR performance [80–82].

MOF-derived bi-metallic sulfide on N, S-codoped porous carbon nanocomposites (NiCo4S@C-1000) prepared by the solvothermal process followed by carbonization at 1000 °C. The prepared materials demonstrated a high ORR activity with a four-electron reduction process. The high ORR activity was related to the high conductivity of the prepared materials and the synergetic effect between the sulfides and the N, S-doped carbon [83]. Co-C@Co9S8 DSNs “Co nanoparticle-embedded carbon@Co9S8 double-shelled nanocages” was prepared by thermal annealing of (ZIF-67) “zeolitic imidazolate framework”@amorphous CoS yolk-shelled structures under inert atmosphere [84]. The Co-C nanocages inside Co9S8 shells acted as active sites for ORR, and the Co9S8 shells protected the Co-C from agglomeration; therefore, a high ORR activity was revealed. Furthermore, the prepared catalyst showed no methanol oxidation activity and, thus, a potential cathode in direct methanol fuel cells (DMFC). It is worth mentioning that the mixed potential at the cathode of the DMFC is one of the main challenges that hindered their development [85,86]. Co@CoS₂@S/N-HCC and Ni@NiS₂@S/N-HCC composites (N-HCC is a nitrogen-doped hollow carbon capsule) were prepared via thermal decomposition of sacrificial MOF nanocrystals coated with a metal–tannic acid coordination polymer shell, followed by pyrolysis in the presence of thiourea to obtain the metal sulfide nanoparticle shell [87]. The high electrical conductivity of the metal sulfide, the high porosity, the hollow morphology, and the role of nitrogen in improving the electrochemical activity resulted in the high ORR activity of the prepared materials. CoS₂@NC “nitrogen-doped porous graphitized carbon-supported cobalt disulfide” was successfully prepared from carbonization of ZIF-67 followed by sulfurization. The prepared material demonstrated high ORR activity, as shown in Figure 9a, that is comparable to that of Pt/C (Figure 9b). The high activity was also related to the aforementioned properties of high electrical conductivity and the role of the nitrogen heteroatom [88].

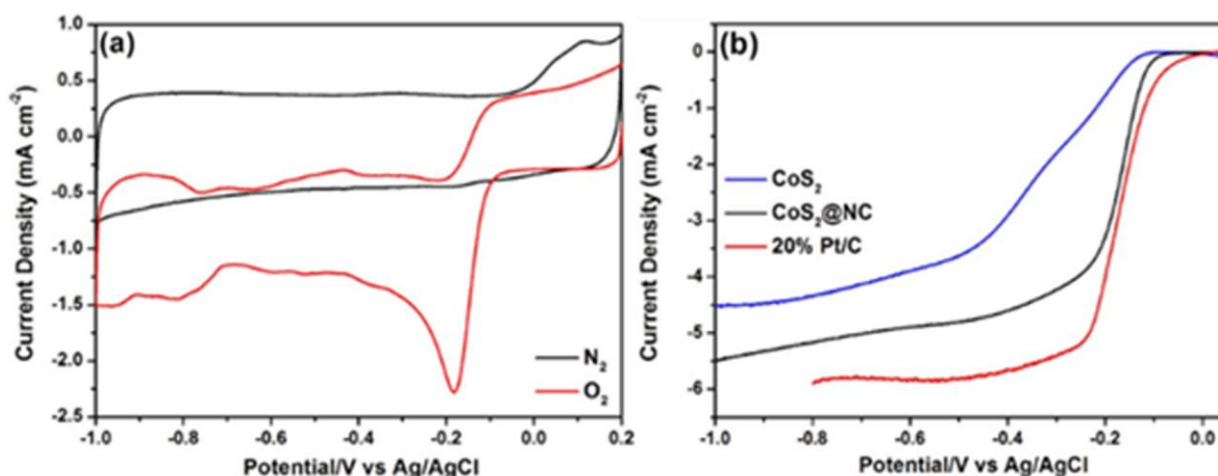


Figure 9. (a) CV of CoS₂@NC under nitrogen and oxygen and (b) ORR polarization curves of CoS₂, CoS₂@NC, and Pt/C @ 1600 rpm [88].

Xiao et al. [80] prepared ZIF-8-derived Fe, N, and S co-doped carbon as ORR catalyst in microbial fuel cells (MFCs). The Fe/S@N/C-0.5 catalyst demonstrated improved reduction kinetics, high durability, and excellent methanol tolerance. The Fe/S@N/C-0.5 catalyst exhibited higher ORR activity than the commercial 20% Pt-C catalyst in both alkaline

and neutral phosphate-buffered saline (PBS) media. Where in 0.1 M KOH solution, the Fe/S@N/C-0.5 manifested a remarkable oxygen reduction potential at 0.861 V (compared to 0.836 V for the Pt/C catalyst) while in 0.01 M PBS solution, the Fe/S@N/C-0.5 catalyst showed the ORR peak at -0.03 V. When tested in air cathode MFC, the Fe/S@N/C-0.5 rendered the cell with an open-circuit voltage (OCV) of 0.71 V, which is higher than 0.63 V for Pt/C-MFC. The maximum power density for the Fe/S@N/C-0.5-MFC is higher than that of the Pt/C-MFC with values of 1196 mW/m^2 and 1137 mW/m^2 , respectively. Therefore, Fe/S@N/C-0.5 is considered a robust catalyst for ORR in MFCs.

Sumin et al. [89] prepared nitrogen and sulfur co-doped porous carbon (NSDPC) electrocatalyst for ORR by impregnation and carbonization using ZIF-8 as a template. The effect of the carbonization temperature and doping densities (controlled by varying the weight ratio between ZIF-8 and thiourea) on the activity of the catalyst was studied. The optimum catalytic performance was obtained at a carbonization temperature of 900°C and a ZIF-8 to thiourea weight ratio of 3. The optimized catalyst NSDPC-3 manifested a desirable specific surface area of $114 \text{ m}^2 \text{ g}^{-1}$, a high ratio of (mesopores + macropores) to (micropores), and a homogenous distribution of N and S atoms. The NSDPC-3 catalyst outperformed the ORR activity of the pristine ZIF-8 and the non-sulfurized samples. Furthermore, it exhibited superior tolerance for methanol crossover and better cycling stability than the commercial Pt/C catalyst. The outstanding performance of the prepared catalyst was attributed to the mesoporous structure and abundant active sites induced by the heteroatom doping process.

S-doped Fe–N–C catalysts were prepared via one-step co-doping by Xiaohui et al. [90]. Co-doping was achieved by in-situ addition of $\text{Fe}(\text{SCN})_3$ during ZIF-8 formation instead of applying the conventional doping approach of physical mixing of the precursor with the already formed ZIF-8. In the one-step approach, $\text{Fe}(\text{SCN})_3$ precursor introduces Fe and S ions simultaneously, where the Zn ions are replaced by Fe without the destruction of the 3D porous structure. This approach led to: (1) creating a catalyst with a very large specific surface area, hence increasing the density of the active sites; (2) augmenting the number of mesopores and micropores that facilitate oxygen diffusion towards the active sites; (3) promoting the activity by S-doping without destruction of the ZIF-8 template structure. The produced catalysts were denoted as Fe-SNC-X, where X represents the volume of the added $\text{Fe}(\text{SCN})_3$ solution in mL. The ORR activity of the Fe-SNC catalysts was high in both acidic and alkaline media and rendered very high stability. In detail, in acidic media of 0.1 M HClO_4 solution, the Fe-SNC-0.45 catalyst had an outstanding ORR activity with a half-wave potential of 0.81 V. While in alkaline media of 0.1 M KOH solution, the Fe-SNC-0.55 catalyst manifested better ORR activity with half-wave potential of 0.92 V which is higher than 0.84 V for the Pt/C catalyst tested under the same condition. The stability of the Fe-SNC catalysts was higher than that of the Pt/C catalyst in both acidic and alkaline environments. Similar results were also observed by Kuixiao et al. [91].

Although Fe-based catalysts demonstrate high ORR activity, their performance degrades with time due to the undesirable Fenton effect [92,93]. Since Co-based catalysts are more stable than Fe-based catalysts, Zunxing et al. [94] prepared a Co-based catalyst with a core-shell structure for the cathode of MFC. The optimum prepared catalyst Co–N/S–C-3.5 exhibited excellent ORR activity and high stability in acidic and alkaline environments. The MFC with Co–N/S–C-3.5 catalyst manifested a performance comparable to that of Pt/C catalyst, where the OCV of the Co–N/S–C-3.5-based MFC was 0.61 V, which is slightly lower than 0.65 V for the Pt/C-based MFC.

The application of sulfurized MOF-derived catalyst is not limited to the cathodic ORR, where it could also be used as an anodic catalyst. Xiang et al. [95] synthesized a 2D sulfurized MOF-derived catalyst for urea oxidation reaction (UOR). The aim of S-doping was to enhance the specific surface area, facilitate mass transport, and increase the exposure of urea to the active sites. The optimized catalyst NiCo-BDC-S-6 manifested high catalytic activity with a lower driving voltage of 1.326 V, which is lower than 1.396 V for the

commercial 20% Pt/C catalyst. Moreover, the NiCo-BDC-S-6 demonstrated high durability; therefore, it is suitable as a UOR catalyst in urea fuel cells.

5. Future Perspective

Some of the reported materials demonstrated superior electrochemical performance, but their synthesization processes were complicated. Therefore, researchers should work on synthesizing MOFs through simple and cost-efficient methods. Moreover, in supercapacitors, only a limited number of publications focused on developing new negative electrodes (anodes). Hence, it is recommended to expand this part of the research in order to enhance the performance of the two electrodes and hence improve the overall performance of the SC. The insulating nature of MOFs restricts their functionality as electrode materials in SCs. Some of the research work summarized here suggested carbon-coating and binder-free synthesis routes, which not only increase the conductivity but also enhance the stability of the electrodes. Yet, further attention should be given to developing solutions for this issue. It has been investigated that the MOFs based on mixed metals (bimetallic and ternary metal) render better performance than the single metal-based MOFs. Researchers may converge on studying the mixed metals and try various organic linkers until solid knowledge is built concerning the effect of increasing the number of metals and varying the type and quantity of both metals and linkers. More experiments and simulations should be conducted to acquire more information about the interface between the electrode and the electrolyte. In addition, clear correlations should be set between the performance of the MOF-based electrodes and the electrolyte's properties, such as the phase of the electrolyte, the pH number, and the operating temperature.

The application of metal chalcogenides-derived MOF, and even MOF itself in fuel cells, is focused on the cathode side as an ORR catalyst, and limited work was conducted at the anode. Therefore, it is recommended to apply chalcogenide-derived MOF in the anode of low-temperature fuel cells such as direct methanol, direct ethanol, and direct urea fuel cells. Moreover, the application of the MOF at the cathode of the fuel cell is also limited to the carbon-derived MOF that is doped with other atoms. Novel and simple methods are required to prepare metal chalcogenides derived MOF and have an ORR activity. Moreover, doping the MOF with carbon materials with a high surface area are worth investigating.

6. Conclusions

The recent progress in metal-organic framework-derived metal sulfides and selenides as electrode materials for supercapacitors (SCs) and as catalysts for fuel cells is summarized in this work. With regards to SCs, the goal for developing both metal sulfide-based and metal selenide-based materials was to synthesize SCs that render high energy densities without sacrificing other electrochemical aspects such as high power densities and cycling stabilities of these SCs.

Many factors should be controlled to increase the stability of the MOF structure and facilitate the ion-accessible specific surface area that leads to increasing the electrochemical performance. These factors include the design of porous MOFs (such as core-shell structures), the loading extent of dopants, the weight ratio between S or Se and metal ions, the method of synthesizing the MOFs on the substrates such as carbon cloth (i.e., is it a binder-free electrode or it used a polymeric binder), and utilization of carbon coating.

On the other hand, for fuel cells, the aim of preparing MOF-derived catalysts was to replace the state-of-art Pt-based catalyst with less expensive catalysts with higher durability and more tolerance to methanol crossover. Some researchers have already achieved this goal by preparing sulfurized catalysts derived from MOF (ZIF-8 was the commonly used one). These catalysts manifested very high specific surface area, excellent catalytic activity, and high stability.

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