Metal Organic Frameworks And Conductive Polymers For Energy Storage

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Abstract

The escalating demand for sustainable and flexible energy storage systems in wearable technology has driven research into advanced electrode materials. This mini-review explores the synergistic potential of metal-organic frameworks (MOFs) and conductive polymers (CPs) as hybrid electrode materials for next-generation smart textiles. While conducting polymers like polyaniline (PANI) and polypyrrole (PPy) offer high conductivity and flexibility, they suffer from mechanical fatigue and instability during cycling. Conversely, MOFs provide ultrahigh surface area and tunable porosity but are limited by poor intrinsic electrical conductivity. The hybridization of these materials creates hierarchical architectures that combine the pseudocapacitive behavior of CPs with the structural regularity of MOFs, significantly enhancing electrochemical performance. This review synthesizes recent progress in synthesis techniques, including in situ polymerization, layer-by-layer assembly, and electrochemical deposition, which are critical for integrating these composites into flexible fibers and fabrics. Detailed analysis of MOF@PEDOT and MOF@PPy hybrids highlights their superior specific capacitance, rate capability, and mechanical robustness under deformation. Despite these advances, challenges such as long-term stability under washing and scalable manufacturing remain significant hurdles. The paper discusses emerging solutions like core-shell nanocoatings and continuous processing methods to address these limitations. Ultimately, this review identifies future research directions for developing durable, high-performance energy storage textiles capable of powering autonomous wearable systems

Keywords

Metal-Organic Frameworks (MOFs), Conductive Polymers, Flexible Supercapacitors, Smart Textiles, Energy Storage, Hybrid Composites, Wearable Electronics, Electrochemical Performance

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1.0 Introduction:

The use of fossil fuels has led to severe environmental challenges, particularly climate change and global warming, thereby accelerating the demand for sustainable and low-carbon energy technologies. Among various solutions, renewable energy sources such as solar, wind, hydro, and biomass have gained prominence; however, their intermittent nature necessitates efficient, reliable, and scalable energy storage systems to ensure a stable power supply [1]. In this context, electrochemical energy storage devices, especially supercapacitors and rechargeable batteries, have emerged as indispensable components for portable electronics, wearable systems, and next-generation smart grids due to their high efficiency, fast response, and design flexibility [2].For advanced energy storage, the performance of the device is largely dictated by the properties of the active electrode materials, which are expected to combine high electrical conductivity, large accessible surface area, mechanical robustness, and chemical stability within a single platform. Conventional materials such as porous carbons, metal oxides, and metal sulfides have been extensively explored, yet they often suffer from intrinsic drawbacks, including limited conductivity, sluggish ion transport, or structural degradation upon cycling, which restrict their practical energy and power densities [3]. These limitations have driven intensive research toward emerging classes of functional materials, particularly conductive polymers (CPs) and metalorganic frameworks (MOFs), and their rationally designed hybrids.

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Conductive polymers, such as polyaniline, polypyrrole, and PEDOT, are attractive for supercapacitor electrodes owing to their high electrical conductivity, tuneable redox activity, and processability into flexible films, fibers, and coatings compatible with textile substrates. They exhibit pronounced pseudocapacitive behaviour, where fast and reversible faradaic reactions at the polymer–electrolyte interface enable high specific capacitance and power capability, making them suitable for lightweight and deformable devices. However, pure CPs often undergo volumetric changes and mechanical fatigue during repeated cycling, resulting in capacity fading and poor long-term stability, especially under bending and stretching conditions relevant to smart textiles [4, 5].

MOFs, composed of metal ions or clusters bridged by organic linkers, offer an exceptionally high surface area, structural diversity, and tuneable pore architecture, making them promising precursors or hosts for energy storage materials. Although pristine MOFs frequently exhibit low intrinsic electrical conductivity, their porous frameworks facilitate ion diffusion and can serve as scaffolds for the growth or confinement of conductive species, thereby enabling hierarchical architectures with improved electrochemical response. By judiciously selecting metal nodes, organic linkers, and post-synthetic modifications, MOF-derived structures can be engineered to balance porosity, conductivity, and mechanical integrity, which are crucial for integration into flexible and wearable devices [6].

Hybridization of CPs with MOFs has recently emerged as a powerful strategy to synergistically couple the pseudocapacitive characteristics of polymers with the high surface area and structural regularity of MOFs. In such composites, the CP component can impart electrical pathways and mechanical flexibility, while the MOF framework enhances ion-accessible surface, stabilizes the polymer chains, and mitigates volumetric changes during cycling, resulting in improved capacitance, rate capability, and cycling stability. Moreover, the morphology of these hybridswhether core–shell structures, interpenetrating networks, or MOF coated fiberscan be finely tuned by controlling parameters such as surfactant type, reactant concentration, reaction temperature, and polymerization time, which directly influence charge transport and ion diffusion [7].

Smart textiles demand energy storage units that are not only electrochemically efficient but also lightweight, breathable, mechanically flexible, and capable of withstanding repeated deformation without performance loss. CP/MOF-based electrodes can be conformally deposited onto fibers, yarns, or fabrics, enabling the realization of flexible supercapacitors that can be woven, sewn, or laminated into garments while maintaining stable operation under bending, twisting, and stretching. Such textile-integrated devices are particularly attractive for powering wearable sensors, health-monitoring systems, and human–machine interfaces, where on-body energy storage must be safe, unobtrusive, and durable [8].

This mini-review focuses on recent progress in the design and fabrication of flexible supercapacitors based on MOFs, conductive polymers, and their composites for smart textile applications. Emphasis is placed on material design principles, hybridization strategies, structure–property relationships, and device-level performance metrics relevant to wearable energy storage. Remaining challenges such as long-term mechanical and electrochemical stability under real-use conditions, large-area scalable processing, washability, and integration with other textile componentsare discussed, together with future research directions toward truly autonomous and multifunctional energy storage textiles.

2.0 Properties of Metal-Organic Frameworks (MOFs)

MOFs offer tuneable porosity, ultrahigh surface areas (>5000 m^2 g^{-1}), and modular structures formed by metal nodes and organic linkers, distinguishing them from conventional porous materials for supercapacitor applications. These features enable precise control over pore hierarchies (micro- to macropores) for rapid ion diffusion and abundant pseudocapacitive sites, with conductivities enhanced via redox-active metals (Ni, Co) or thiophene linkers. Diverse routes solvothermal, microwave-assisted, or mechanochemical allow substitution of nodes/ligands, nanosizing, or flexible linker incorporation to boost mechanical resilience against cycling-induced volume changes, critical for textile electrodes. Derivatives like MOF-derived carbons or thin 2D nanosheets (<10 nm thick) further optimize electron pathways while preserving hierarchical porosity [9].Despite advantages in ion-accessible surfaces, pristine MOFs face poor intrinsic conductivity (<10-6 S cm^{-1}), pore collapse under repeated charge–discharge, and pH sensitivity, limiting capacitances to 100-500 F g^{-1} and cycling retention. Stability improves with high-valent metals (Zr4+) paired to hard bases or divalent soft ions, alongside scalable, low-cost synthesis from mineral salts. Hybridization with conductive polymers addresses these gaps, synergistically enhancing rate capability (>90% retention over 5000 cycles) and flexibility for smart textiles.

3.0 Synthesis Techniques for MOF–Polymer Composites

In situ polymerization, layer-by-layer (LbL) assembly, and electrochemical deposition enable intimate integration of MOFs with conductive polymers (CPs) like polyaniline (PANI), polypyrrole (PPy), or PEDOT, ensuring uniform coatings, hierarchical porosity, and synergistic conductivity enhancement for flexible supercapacitors.

3.1.1 In Situ Polymerization

MOF crystals serve as templates where monomer polymerization occurs directly on surfaces or within pores, yielding core–shell or interpenetrating CP@MOF architectures. Parameters such as oxidant concentration (e.g., APS for PANI), pH, temperature (20–80°C), and reaction time (1–24 h) control polymer thickness (10–100 nm) and loading, boosting specific capacitance by 2–3× (e.g., PPy–ZIF-67 hybrids achieving 650 F g^{-1}) while mitigating MOF brittleness [10].

3.1.2. Layer-by-Layer Assembly

Alternating deposition of anionic MOF nanosheets and cationic polymer layers via electrostatic interactions produces freestanding films (5–50 nm per bilayer) with precise thickness control and >90% capacitance retention after 5000 bends. Ideal for textiles, this method preserves MOF porosity (BET >2000 m2g^{-1}) and imparts CP-mediated conductivity (>10 S cm^{-1}), as demonstrated in PANI–UiO-66 membranes [11].

3.1.3. Electrochemical Deposition

One-step electro-polymerization on MOF-coated electrodes or conductive fabrics yields conformal CP coatings (20–200 nm) with tailored pseudocapacitive sites. Cyclic voltammetry (-0.2 to 1.0 V) or chronoamperometry optimizes film uniformity, enabling fiber-shaped devices with 300–500 F g^{-1} and stability under 180° bending [12].

3.1.4 Diffusion Method

The diffusion method gradually transports reactants into contact to promote controlled crystal growth, primarily yielding single crystals suitable for X-ray diffraction analysis, especially for low-solubility MOFs. In solvent liquid diffusion, two density-stratified layers precipitant solvent and product-laden solventare separated by an intermediate solvent layer; crystals nucleate at the interface as the precipitant diffuses slowly. Alternatively, physical barriers (e.g., nested vials) or gels slow diffusion further, preventing bulk precipitation and enabling high-quality MOF nucleation for composite precursors [13].

3.1.5 Hydrothermal/Solvothermal Method

Hydrothermal/solvothermal synthesis drives self-assembly of MOFs from soluble precursors in sealed autoclaves under autogenous pressure (80-260°C), with cooling rate dictating crystallization kinetics. Though reaction times span days to weeks, this approach excels in morphological control, producing uniform nanocrystals ideal for polymer infiltration or coating in composites. Microwave assistance accelerates the process to hours, generating seeding conditions akin to solvothermal routes while enabling precise tuning of particle size and shape for scalable supercapacitor electrodes [14].

3.1.6 Electrochemical Method

Electrochemical synthesis generates MOFs directly on conductive supports by in situ metal ion release, bypassing aggressive anions (e.g., nitrates) and enabling rapid, low-temperature (<solvothermal) growth with minimal thermal cracking from mismatched expansion coefficients. Voltage tuning or pulsed signals fine-tune nucleation near the substrate, reducing bulk aggregation and favouring thin films or membranes for polymer hybridization. This industrially viable route produces phase-pure MOF powders or coatings with hierarchical porosity, enhancing CP integration for flexible textiles.Microwave-assisted in situ growth accelerates synthesis (<30 min) for scalable CP–MOF yarns; 3D printing extrudes MOF–PEDOT inks into porous architectures; and plasma-enhanced polymerization grafts ultrathin CPs onto MOFs for breathable textiles. These innovations achieve >85% retention over 10,000 cycles and areal capacitances >1 mF cm^{-2}, addressing scalability for smart wearables.

3.2 MOF@CP Hybrid Strategies

MOF@CP hybrids integrate metal–organic frameworks with conductive polymers through strategies that maximize interfacial synergy, preserving MOF porosity while enhancing conductivity and mechanical flexibility for textile supercapacitors. These methods address CP volumetric instability during cycling and MOF powder processability, yielding freestanding electrodes with π–π-stabilized charge transport.

3.2.1 MOF Hybrids with Poly(3,4-ethylenedioxythiophene) (PEDOT)

PEDOT stands out for its exceptional conductivity (up to 1000 S cm^{-1}), optical transparency, and stretchability (>4% strain), making it highly suitable for flexible MOF hybrids in smart textile supercapacitors. Hybrids leverage PEDOT's film-forming ability to create binder-free, breathable electrodes with enhanced cycling stability and rate performance.

Table.1.Supercapacitor performance of MOF@PEDOT hybrids and their comparison of electrochemical properties.

Hybrid material	Gravimetric/ Areal Capacitance	Current density/ Scan rate	Capacity retention (cycles)	Energy density/ Power density	Electrolyte (Potential window)	Ref
PEDOT:PSS@ HKUST-1	31 F g^{-1}	1 A g^{-1}	90.1 % (10 000) at 0.2 A g^{-1}	-	1M Na_2SO_4 (0.35 V)	15
UiO-66/GO/CNTF/ PEDOT	30 mF cm^{-2}	5 mV s^{-1}	89% (1000)	0.0022mWh cm^{-2}; 0.2 mW cm^{-2} at 0.4 mA cm^{-2}	PVA/H_3PO_4 (1 V)	16
HKUST-1/GO/CNTF/PEDOT	37.8 mF cm^{-2}	5 mV s^{-1}	89.8% (2000)	0.051 mWh cm^{-3}; 2.1 mW cm^{-3} at 0.4 mA cm- 2	PVA/H_3PO_4 (1 V)	17

Table 2. Electrochemical Performance of Selected MOF@PPy Hybrids

Hybrid material	Gravimetric/ Areal Capacitance	Current density/ Scan rate	Capacity retention (cycles)	Energy density/ Power density	Electrolyte (Potential window)	Ref
PPy–CPO-27- NiPPy–CPO-27- CoPPy–HKUST-1	354 F g^{-1} 263 F g^{-1} 185 F g^{-1}	-	42.3% (2500) 68.3% (2500) 27.1% (2500)		1 M KCl (1 V)	18
PPy@UIO-66@CT	565 F g^{-1}	0.8 mA cm- 2	90% (500)	38.2 Wh kg^{-1}; 37.7 W kg- 1	1 M H2SO4/0.4 M hydroquinone (0.8 V)	19
Cu-TCPP/PPy	240 F g^{-1}	2 A g^{-1}	68.5% (3000) 5 A g^{-1}	0.29 mWh cm^{-3}; 270 mW cm^{-3}	PVA/H2SO4 (0.9 V)	20
(NiCo-MOF@PPy)//AC	132 F g^{-1}	0.5 A g^{-1}	79.1% (10 000)	41.2 Wh kg^{-1}; 375 W kg^{-1}	2 M KOH (1.5 V)	21
Cu-CAT -NWAs/PPy	252.1 mF cm^{-2}	1.25 mA cm^{-2}	90% (8000) at 100 mV s- 1	22.4 µWh cm^{-2}; 1.1 mW cm^{-2}	LiCl/PVA gel electrolyte (0.8 V)	22

3.2.2 MOF Hybrids with Polypyrrole (PPy)

Polypyrrole (PPy) is widely employed in MOF hybrids due to its facile electro-polymerization, high pseudo-capacitance (from reversible redox), and biocompatibility, effectively enhancing MOF conductivity and mechanical adhesion to textiles. PPy coatings (20–150 nm) suppress MOF collapse while enabling flexible, aqueous-stable electrodes with improved rate capability.

4.0 Challenges and Opportunities in MOF-Based Smart Textiles

MOF@CP hybrids face critical hurdles for practical smart textile deployment, including cycling-induced structural degradation, limited intrinsic conductivity, and processing scalability. Opportunities lie in targeted material engineering and manufacturing innovations to unlock commercial viability. Stability Challenges: Repeated deformation and laundering cause MOF pore collapse and CP delamination, reducing capacitance by 20–40% after 5000 wash cycles; aqueous electrolytes exacerbate linker hydrolysis in acid/base conditions. Mechanical fatigue under >30% strain leads to microcracks, compromising breathability and skin comfort. Scalability Barriers: Lab-scale solvothermal synthesis yields grams, not kilograms; high-cost linkers (e.g., BTC >\$50 kg^{-1}) and solvent-intensive processes hinder textile-yardage production. Uniform coating over km-scale fabrics remains inconsistent, with edge effects causing 30% performance variation. Conductivity and Metrics Gaps: Bulk MOF conductivity (<10^{-5} S cm^{-1}) demands >30 wt% CP, diluting capacitance density; areal metrics lag textiles (<1 mF cm^{-2} vs. >5 mF cm^{-2} needed). Energy density (20–50 Wh kg^{-1}) falls short of Li-batteries for all-day wearables.Emerging Solutions: Core–Shell Nanocoating: Atomic layer deposition of hydrophobic silanes protects MOFs, achieving 95% capacitance retention post-100 laundry cycles.Continuous Roll-to-Roll Processing: Microwave/plasma-assisted synthesis coats 100 m fabrics/min at <10% cost premium.Conductive MOF Engineering: Thiophene-linker or Ni/Co-node doping reaches 10 S cm^{-1}, minimizing CP loading to 10 wt%.

5.0 Conclusion

This paper reviews the latest breakthroughs in MOF–conductive polymer research, offering strategies for designing and optimizing materials tailored for wearable energy storage systems. These insights aim to drive innovation in next-generation smart textile technologies. Comparative research on synthesis techniques and their outcomes can clarify the mechanisms behind hybridization improvements. Several strategies exist to enhance current materials. One approach involves novel conductive MOFs, particularly bimetallic variants with superior electrochemical properties. Another focuses on CP nanostructures (dendrimers, nanofibers, nanotubes) that provide higher surface area and optimized MOF/CP/electrolyte interfaces. These advances may necessitate new MOF@CP preparation methods. Further research should maximize CP mechanical properties to create robust, bendable, stretchable materials for organic electronics. Finally, practical efforts must prioritize long-term stability and durability testing to enable market-ready MOF@CP hybrids.

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