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# *Covalent Organic Frameworks in Energy Storage Devices*

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***Abstract.*** With the aim of carbon neutrality, there are serious problems in the supply of lithium resources and inherent safety risks of traditional lithium-ion batteries that are hindering the green development of the energy-storage industry. Porous Crystalline Polymers with tailored structures called Covalent Organic Frameworks (COFs) have been developed to address various problems in industry. Two general synthetic Strategies are given. Traditional solvothermal synthesis of COF powders has good crystallinity but is energy-intensive and produces a large amount of pollutants. Electrochemical Polymerisation is a relatively simple way to prepare flexible COF thin films. Modifying the pore channel and active site of functionalised COFs to build single-ion solid-state electrolytes with high room-temperature ionic conductivity and suppress the growth of lithium dendrites has been achieved. Long-cycle lithium-ion battery anodes have been prepared by covalent bonding with MXene; redox-active COFs are also good supercapacitor materials. Polyimide COF films can also be employed in energy storage and electrochromism for the development of flexible wearable energy-storage devices. Although they have a low intrinsic electrical conductivity, COFs are still used in some places. By reasonably modifying the molecule and regulating the interface, it will be a good material for the next generation of high-performance energy-storage devices.

***Keywords:*** electrochemical, low-carbon, flexible, energy storage, lithium battery

## 1. Introduction

With the world's pursuit of carbon neutrality, there is an increasing demand for lithium-ion batteries, and according to the International Energy Agency, lithium consumption will rise by 350% by 2040 [1]. There is now a significant shortfall in resources for the construction of green buildings. Traditional liquid batteries have flammable organic electrolytes and are thus prone to leakage and thermal runaway; their energy density is also close to the physical limit. Therefore, many all-solid-state lithium batteries with solid polymer electrolytes have shown good safety performance and are thus popular choices. The room-temperature ionic conductivity of the traditional poly (ethylene oxide)-based electrolyte is too small; thus, it is not used [2].

Covalent organic frameworks have recently begun to be used in new energy storage. Crystalline porous polymers are made up of light organic building blocks connected by strong covalent bonds in

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an organised way to form two-dimensional or three-dimensional structures. Since their discovery, they have gained the attention of many scholars due to their permanent porosity, large surface area, regular and adjustable nanochannels, and fine molecular-level designability. In fact, they are metal-free and completely organic; therefore, they meet the requirements for green chemistry and low-carbon production of sustainable devices.

They have a good structure for solid electrolytes. Periodic one-dimensional channels are long-range organised roads that can transport lithium-ion rapidly by decoupling ion migration from the slow motion of polymer chains. Anionic or Lewis basic sites can be added to the pore walls to promote salt dissociation and reduce the ion-hopping barrier. Two-dimensional COFs are inherently soft and thus can prevent the formation of damaging lithium dendrites and buffer the volume expansion of the electrode material with age [3]. Soft materials are being used to develop wearable electronic devices that are comfortable for people to wear and have a long service life.

There are still some serious issues; for example, if there is poor contact between the COF fillers and the polymer matrix, it will be disorderly aggregated, hinder ion transport, and reduce mechanical properties. Design Ideas and Synthesis Methods for COFs, the latest developments in solid electrolytes, and future directions of structure-activity relationships to promote sustainable, low-carbon, flexible and circular energy systems will be introduced in this paper [4].

## 2. Covalent organic frameworks (COFs)

### 2.1. Basic properties of COFs

Covalent organic frameworks are a class of crystalline porous materials constructed from light elements (C, H, O, N, etc.) via reversible covalent bonding [5]. With designable building units and precisely tunable pore structures at the molecular level, COFs can be functionalized by grafting redox-active groups or heteroatoms into the backbone, giving them high application flexibility in electrochemical energy storage systems. However, the fully organic skeleton of pristine COFs has limited electron delocalization, resulting in intrinsically low electrical conductivity, which restricts their direct application in high-rate electrochemical devices.

### 2.2. Typical preparation methods

Solvothermal synthesis and electropolymerization are the two most widely used preparation routes for COF-based energy storage materials, with distinct technical characteristics and applicable scenarios [6].

#### 2.2.1. Solvothermal method

The solvothermal method is the classical route for preparing COFs with high crystallinity and long-range ordered pore structures. The reaction proceeds in a sealed reactor under elevated temperature, where reversible covalent polycondensation (e.g., Schiff base reaction) takes place under thermodynamic equilibrium, allowing gradual crystal nucleation and defect healing. For example, using melamine and terephthalaldehyde as building blocks, a highly regular three-dimensional COF can be obtained via solvothermal reaction in dimethyl sulfoxide with acetic acid as the catalyst, achieving a specific surface area of up to 546.0 $m^2$ $g^{-1}$ Its well-developed porous structure provides abundant adsorption and coordination sites for lithium ions [2]. On this basis, $Ti_3C_2$ MXene can be

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introduced in situ during the solvothermal process, and covalent bonding between the two phases is realized through silane coupling agents to build an efficient electron transport network (Figure 1).

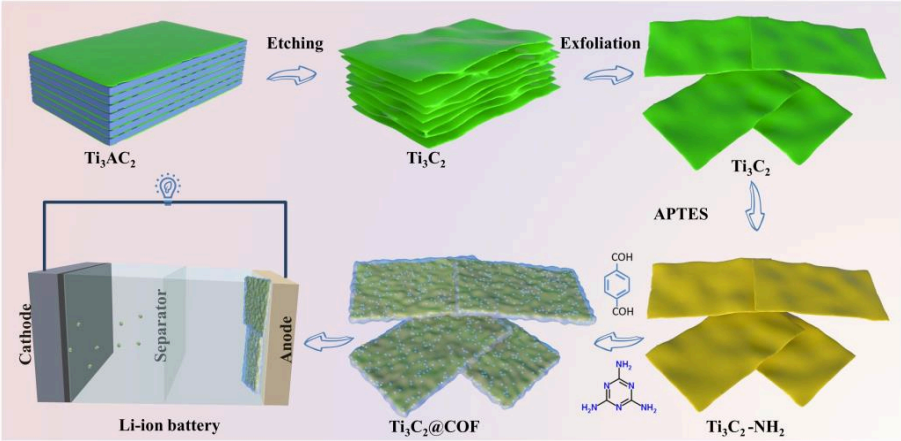


Figure 1. Schematic illustration of the solvothermal synthesis of Ti3C2@COF composite [2]

This method is suitable for preparing powder COF materials with well-defined pore structures, and is widely used in laboratory fundamental research. Its core limitation is the long reaction cycle (usually several days) and high consumption of high-boiling organic solvents; the products are mostly insoluble powders and cannot be directly processed into continuous thin films.

### 2.2.2. Electropolymerization method

Electropolymerization is an efficient film-forming route developed in recent years, which drives monomer polymerization on the electrode surface through applied potential. The reaction proceeds at room temperature without harsh high-temperature and high-pressure conditions, and the process can be regulated by adjusting electrical parameters. COF films prepared by this method grow in situ on the substrate with tight interfacial contact, and no additional binders are required for subsequent device assembly.

This method excels at preparing freestanding COF thin films directly on conductive substrates, and is compatible with flexible device processing. Its main limitation is that polymerization is confined to the electrode surface, and the product crystallinity is generally lower than that of solvothermal samples, making it difficult to prepare bulk COF materials with high crystallinity.

Despite its clear advantages in crystal structure control and pore architecture, the solvothermal method suffers from notable drawbacks in industrial scale-up: reaction cycles typically last several days and consume large quantities of high-boiling-point, difficult-to-recover organic solvents, accompanied by considerable environmental pressure. Moreover, the products are mostly insoluble powders that cannot be directly processed into continuous thin films. Meanwhile, the intrinsically limited electron delocalization of pure organic COF frameworks results in poor electrical conductivity, leading to unsatisfactory rate performance when directly used as electrodes [7]. To address this, current studies commonly adopt an in-situ introduction of $Ti_3C_2$ MXene into the solvothermal system, achieving covalent bonding between the heterogeneous phases via silane coupling agents to construct efficient electron transport networks.

Overall, this route remains confined to fundamental mechanistic research at the laboratory scale and is difficult to directly translate into large-scale industrial capacity.

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## 3. Applications of COFs in lithium-ion batteries

Benefiting from precisely tunable pore structures at the molecular level and abundant designable redox-active groups, COF materials show high functional designability. They can be used either as independent active electrode materials, or constructed into composite structures with two-dimensional MXene, and can also serve as ion transport frameworks in solid electrolytes, adapting to different application requirements such as high-capacity anodes and high-safety solid-state battery systems. The molecular design strategies for different application scenarios differ significantly [7].

### 3.1. Electrode material applications

Pristine COFs suffer from intrinsically low electrical conductivity due to limited electron delocalization of organic skeletons, which restricts their direct application as battery electrodes. Covalent compounding with $Ti_3C_2$ MXene is an effective modification strategy to construct high-performance lithium-ion battery anodes. In a typical route, $Ti_3C_2$ MXene is first amino-functionalized with APTES, and then undergoes in-situ covalent polycondensation with aldehyde-functionalized COF precursors to form a $Ti_3C_2$@COF heterostructure. The covalent bonding at the interface effectively reduces interfacial impedance between the two phases, and the regular pore cavities inside the COF provide abundant lithium storage sites.

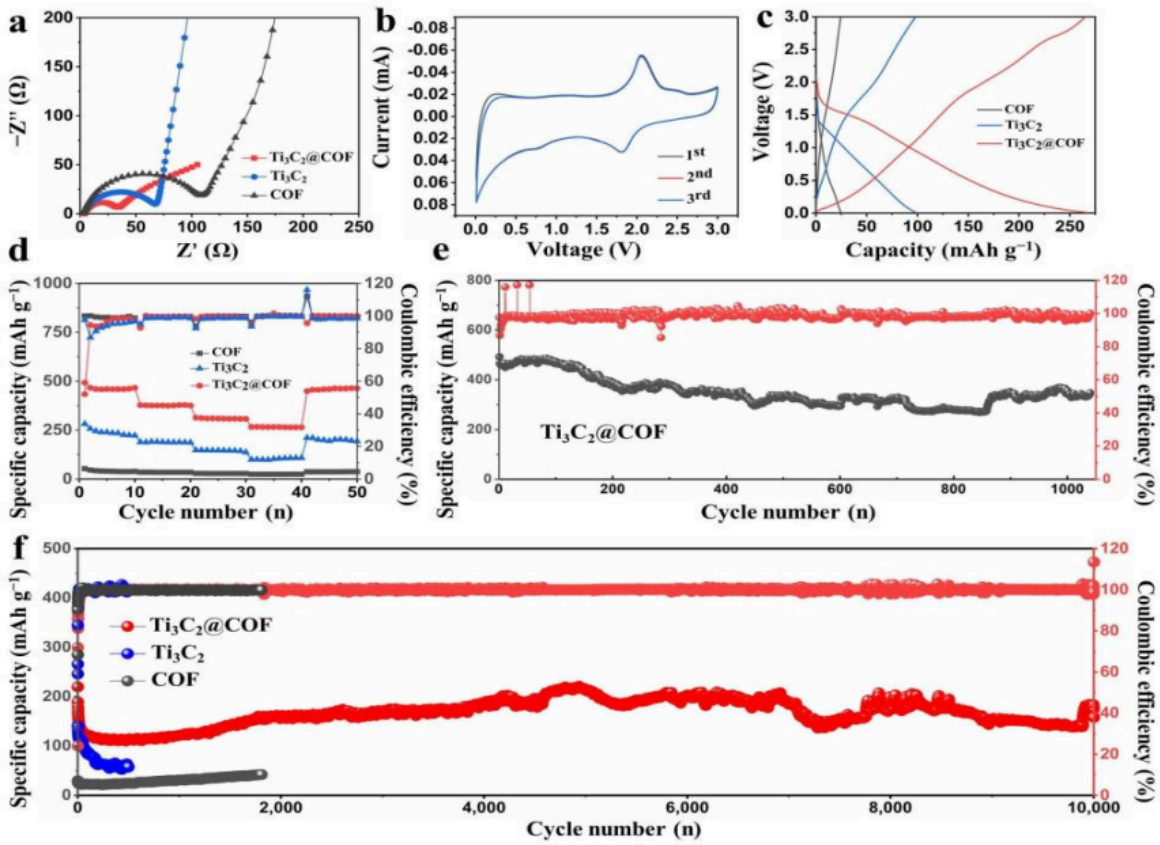


Figure 2. Electrochemical performance of electrode materials: (a) EIS curves of COF, Ti3C2@COF, and Ti3C2 electrodes; (b) CV curves of Ti3C2@COF electrode; (c) Galvanostatic charge-discharge curves; (d) Rate performance of the COF, $Ti_3C_2$@COF, and Ti3C2 electrodes; (e) Long-term cycling stability of Ti3C2@COF electrode at 0.1 C; (f) Cycling stability test of COF, Ti3C2@COF, and Ti3C2electrodes at 1 A g-1 [3]

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As the electrochemical test results showed in Figure 2 that the composite electrode delivers a specific capacity of 490 mAh $g^{-1}$ at a current density of 0.1 A $g^{-1}$. After 10,000 stable cycles at 1 A $g^{-1}$, it still retains a specific capacity of 180 mAh $g^{-1}$. The energy storage process is dominated by a pseudocapacitive mechanism, and its rate performance is significantly better than that of pure COF and pure MXene electrodes [3].

### 3.2. Solid-state electrolytes and interface regulation

Traditional liquid lithium batteries have potential safety risks such as electrolyte leakage, thermal runaway and lithium dendrite penetration. All-solid-state lithium metal batteries are the core development direction of next-generation high-safety energy storage systems, but commercial polymer electrolytes generally have insufficient room-temperature ionic conductivity, which is difficult to meet practical application requirements.

Recent studies have constructed a layered single-ion conductor electrolyte (PEI@TpPa-$SO_3Li$) by interpenetrating polyethyleneimine (PEI) into sulfonated COF nanosheets. The electrostatic interaction between the amino groups on the PEI chain and the sulfonate groups on the COF framework induces directional alignment of the pore channels, forming continuous $Li^+$ hopping pathways along the pores. This structure achieves an ionic conductivity of $1.4 \times 10^{-4}$ S $cm^{-1}$ at 30 ℃ and a high lithium-ion transference number of 0.95, which effectively reduces concentration polarization during cycling [8].

Meanwhile, the PEI-interpenetrated structure significantly improves the mechanical strength of the electrolyte, with a Young's modulus of 408.7 MPa, which can physically inhibit the growth of lithium dendrites at the electrode-electrolyte interface. When assembled into half-cells with LFP and NMC cathodes respectively, the capacity retentions reach 98% and 88% after 300 cycles at 30 ℃ and 0.2 ℃. As it can be seen in Figure 3, the electrolyte has an electrochemical stability window of 0 – 4.7 V, which is compatible with high-voltage ternary cathode systems and shows good application potential [4].

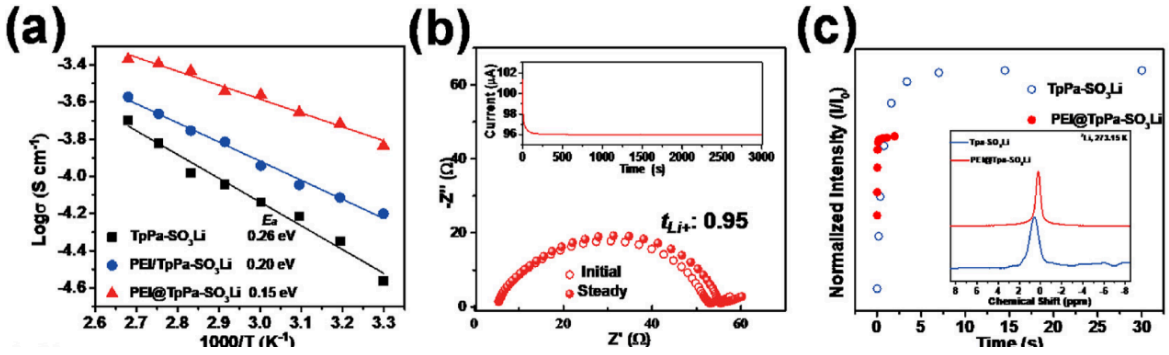


Figure 3. (a) Temperature-dependent conductivity of TpPa-SO3Li, PEI/TpPa-SO3Li, and PEI@TpPa-SO3Li electrolytes (ionic conductivity (s)); (b) Li+ transference number of PEI@TpPa-SO3Li electrolyte; (c) Saturation recovery plots of TpPa-SO3Li and PEI@TpPa-SO3Li electrolytes from MAS7Li NMR spectra [4]

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## 4. Applications of COFs in supercapacitors and flexible devices

### 4.1. Supercapacitor electrodes

With ordered ion transport channels and easily functionalized organic skeletons, COFs also have good application prospects in the field of supercapacitors. A typical imine-linked conjugated COF constructed from triphenylamine and terephthalaldehyde building units is a representative example for capacitive energy storage [9]. Its permanent ordered pore structure provides unobstructed diffusion paths for electrolyte ions, and the redox-active amine groups in the skeleton can provide additional pseudocapacitance.

In a three-electrode test system with aqueous electrolyte, the COF electrode delivers a specific capacitance of 231 F $g^{-1}$ at a current density of 0.5 A $g^{-1}$. After 5000 galvanostatic charge-discharge cycles, it maintains 91% of the initial capacitance, showing good cycling stability as an electrode material for supercapacitors [9].

### 4.2. Flexible energy storage devices

The electropolymerization method supports the in-situ growth of COF films directly on flexible conductive substrates such as PET-ITO without additional binders, which simplifies the fabrication process of flexible electrodes. The prepared COF-based flexible devices can maintain stable energy storage performance under repeated bending, cutting and other deformations, and can integrate electrochromic function on the basis of energy storage without complex process adjustment. Such materials have broad application prospects in wearable electronic devices and flexible smart energy storage windows [10].

## 5. Current challenges and development prospects of COFs

### 5.1. Bottlenecks in the development of COFs

Based on existing literature, four core limitations hinder the industrialization of COFs. First, pure organic COFs possess weak intrinsic electron delocalization and poor conductivity, necessitating compositing with MXene or carbon-based conductive materials, which increases process complexity and production costs [11]. Second, all current synthetic routes have shortcomings: solvothermal methods are highly polluting and energy-intensive, electropolymerization can only produce thin films, and biomass-derived products suffer from insufficient crystallinity—none are suitable for large-scale industrial production. Third, under long-term battery cycling, organic frameworks are prone to structural collapse, persistent side reactions occur at electrode/electrolyte interfaces, and the pore architecture of solid-state electrolytes becomes disordered after prolonged operation, causing continuous capacity decay. Fourth, existing COF synthesis relies heavily on expensive fossil-derived monomers, biomass modification processes remain cumbersome, and a complete "synthesis–degradation–monomer recovery" closed-loop system has yet to be established, resulting in inadequate sustainability [12].

### 5.2. Future directions

To address the problems mentioned above, future research on COF-based energy-storage materials can be carried out in the following five directions: First, continuous green synthesis processes should be developed by optimising mechanochemical, aqueous-phase and scalable

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electropolymerisation routes; enhance the structural rigidity of biomass monomers to improve the crystallinity of bio-based COFs; and reduce both pollution and cost [13]. Second, to create a fully conjugated, heteroatom-doped COF with high intrinsic conductivity, design a molecular backbone, simplify the in-situ covalent compositing with MXene, and fully expose the redox-active sites [14]. Third, improve the engineering of interfaces by designing covalently bonded heterogeneous electrodes and ordered single-ion conducting solid electrolytes to reduce side reactions at the interface, suppress lithium dendrites, and extend the cycle life of the battery. Fourth, develop multi-functional integrated devices that combine energy storage, electrochromism and ion sieving for new flexible wearable applications. Finally, establish a closed-loop industrial chain for biomass-based COFs to achieve low-carbon operation at all stages of the raw material extraction, material preparation and degradation recycling process, in line with the goals of the dual-carbon strategy [15].

## 6. Conclusion

COFs have a regular pore structure and tunable molecular structure, so they are suitable for many applications in electrochemical energy storage.

The traditional solvothermal synthesis method for producing highly crystalline COF powder has a low yield, so we can use electrochemical polymerization to generate flexible COF films in situ that are suitable for all sorts of devices.

COF/MXene heterostructures have been used as high-performance lithium-battery anodes; functionalised COFs can form ordered ion-transport pathways in solid electrolytes and have good room-temperature conductivity and effective suppression of lithium dendrites. COFs are also good materials for supercapacitors and flexible power sources.

However, because of their low intrinsic conductivity, it is difficult to carry out large-scale synthesis and maintain the long-term structural stability of COFs for broad application. In the future, research will be carried out to construct conjugated backbones, develop efficient and scalable synthesis methods, improve interfacial compatibility, etc., in order to expand the screening of materials and advance the development of devices for high-safety solid-state batteries and next-generation flexible energy storage systems based on COFs.

## Author contribution

All the authors contributed equally and their names were listed in alphabetical order.

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