WEP
Warwick
Evans
Publishing

Transactions on Environment, Energy and Earth Sciences
ISSN: 2960-1924, eISSN: 2960-2300 | Volume 5
EMCEME 2025

Covalent Organic Frameworks as Electrode Materials for lithium-ion batteries

Lijia Zheng*

College of Chemistry and Materials Science, Fujian Normal University, Fuzhou, China

*Corresponding author: 107062022068@student.fjnu.edu.cn

Abstract. As renewable energy expands and the electric vehicle market grows, Lithium-ion batteries (LIBs) are playing an increasingly pivotal role in the energy storage sector. Covalent Organic Frameworks (COFs), as an emerging functional material, have widespread applications across various fields. They are viewed as promising electrode candidates for rechargeable batteries because they offer large surface areas, tunable pore structures, high porosity, and facile surface functionalization. This review summarizes recent progress on COFs for lithium-ion battery electrodes. It examines structural design approaches and functional modifications that enhance electrochemical behavior. It also analyzes the mechanisms by which COFs improve battery performance, for example by facilitating ion transport and by increasing electron conductivity through tailored architectures. The review addresses both cathode and anode uses of COFs, and it highlights recent experimental advances and comparative evaluations across material classes. Finally, it identifies current technical challenges such as synthesis scale-up, intrinsic conductivity limits, pore-conductivity tradeoffs, and interface stability, and it outlines directions for future work to advance COF-based electrodes toward practical implementations.

Keywords: lithium-ion batteries; Covalent Organic Frameworks; electrode materials.

1. Introduction

With the rapid growth of the global population, accelerated economic development, and adverse climatic changes, the consumption of fossil fuels has surged dramatically. To address energy and environmental challenges, the quest for convenient, clean, and efficient energy storage solutions has become a critical priority. As a vital component of energy storage technologies, battery systems have achieved remarkable advancements over recent decades. In particular, the widespread adoption of lithium-ion batteries (LIBs) has enabled the proliferation of electric vehicles, portable electronics, and renewable energy integration. Currently, LIBs dominate electric vehicle powertrains due to their high energy density and mature manufacturing processes, with over 95% of electric vehicles relying on LIBs for power [1]. However, conventional electrode materials—primarily inorganic transition metal oxides (e.g., NCM ternary materials) and graphite—face challenges such as resource scarcity (cobalt, nickel), theoretical capacity limitations, and thermal runaway risks, alongside concerns over high recycling costs and potential environmental pollution. To overcome these bottlenecks, researchers are actively exploring novel materials to enhance battery performance.

COFs represent a novel class of porous crystalline materials, constructed through the covalent linkage of organic monomers, exhibit high designability, extremely high surface area, and structural stability. Due to their unique structure, covalent organic frameworks (COFs) have been widely studied in areas such as gas adsorption and storage, catalysis, separation and sensing, biomedical applications, and optoelectronic materials. Recently, scientists have discovered that COFs, by utilizing their distinctive porous networks and tunable redox properties, display unique advantages in the energy storage field, particularly for use as electrode materials in lithium-ion batteries.

The synthesis and structural design strategies of COFs are the subject of numerous review studies. Numerous studies investigate the use of COFs in lithium-ion batteries and other batteries such as lithium metal and sodium-ion batteries. The benefits and difficulties of employing COFs in lithium-ion battery electrode materials are not well covered in overviews, nevertheless. Therefore, this review briefly summarizes the latest applications of COFs in lithium-ion batteries. The article first introduces the basic structure and working principles of COFs Electrode Materials. It then presents the recent advancements in using COFs as cathode and anode materials for lithium-ion batteries. Finally, it discusses the challenges, prospects, and improvement strategies for COF electrodes.

2. COFs Electrode Materials

A new family of porous crystalline materials called covalent organic frameworks (COFs) is made up of organic monomers joined by covalent bonds. They exhibit high tunability, exceptionally large specific surface areas, and robust structural stability. By altering the geometry of the building blocks, various COF architectures can be synthesized. COFs are generally categorized into two-dimensional (2D) and three-dimensional (3D) frameworks. The topologies of 2D COF networks include triangular, diamond, square, and hexagonal configurations, with hexagonal arrangements being the most prevalent in 2D COFs [2, 3]. Hexagonal channels often form when linearly symmetric monomers connect in groups of three. By adjusting reaction conditions such as time, temperature, and solvent, 3D COF frameworks can adopt various morphologies, including nanosheets, nanorods, nano- or microspheres, and nanowires.

The charge storage processes of COF-based electrodes rely on reversible changes of redox-active organic groups or of partial charge states within the framework [4, 5]. Organic electrode materials tend to fall into two primary categories based on the species' charge state during redox reactions: Organics of types n and p [6]. P-type organics undergo oxidation to produce positively charged cations in these reactions, while n-type organics undergo reduction to produce negatively charged anions. Most common COF electrode materials fall into the n-type category. COF electrodes store and release charge through a combination of ion transport within ordered pores and redox reactions at functional sites on the framework. The regular nanoscale channels of COFs provide pathways for electrolyte ions to access internal surfaces. Electron transport is enabled by the framework's π-conjugated system, or, when the intrinsic conductivity is insufficient, by conductive additives that form continuous electronic pathways. During charge and discharge, electrons travel through the conductive network while ions migrate within the pores to maintain charge neutrality. The reversible potential and the capacity are influenced by the density of active sites, the energy distribution of those sites, the degree of electronic delocalization, and the ion-accessible surface area. Thus, COF electrodes can be viewed as porous organic scaffolds that host embedded redox-active sites.

3. COFs as cathode materials in LIBs

During the charging process, cathodes release lithium (Li) to the anode through the electrolyte. In the discharging process, they absorb Li from the anode. Cathodes are key components of lithium-ion batteries and significantly influence both energy density and cost. Currently, most cathode materials are inorganic compounds, such as phosphates and layered oxides. These inorganic materials often undergo substantial volume expansion during battery cycling. This expansion causes a noticeable decrease in the battery's reversible capacity [7]. For instance, commercial cathode materials like $LiFePO_4$ possess a theoretically calculated specific capacity of 170 $mAh\cdot g^{-1}$, while $Na_2Fe(SO_4)_2$ offers 91 $mAh\cdot g^{-1}$. Conversely, commercially available graphite anodes exhibit a specific capacity of 372 $mAh\cdot g^{-1}$. This substantial discrepancy impedes the further enhancement of battery energy density and represents a significant barrier to the advancement of lithium-ion battery technology. [8]. Therefore, developing new cathode materials with higher specific capacities is extremely urgent.

Compared to traditional lithium-ion battery cathode materials such as phosphates and layered oxides, COF-based cathode materials offer several advantages. COFs are highly porous and have large surface areas. They can change the size of their pores. They can include different functional groups. These characteristics improve cathode electrochemical performance [9]. In recent years, research on covalent organic frameworks (COFs) as cathode materials for lithium-ion batteries has advanced clearly and steadily. Early studies show that many COF-based cathodes have low intrinsic electronic conductivity and limited specific capacity tied to individual redox sites. To address these problems, researchers have developed several practical strategies. One strategy introduces multiple redox-active groups into the COF network to raise theoretical capacity and to widen the range of redox potentials. Another strategy makes composites by mixing COFs with conductive additives, for example carbon nanotubes or graphene, so continuous electron pathways form and charge transport improves. Researchers also build extended π-conjugated backbones and highly conjugated linkages to increase electron delocalization and so enhance conductivity. These combined approaches have produced clear gains in the electrochemical behavior of COF-based cathodes, including higher reversible capacity, better rate performance, and improved capacity retention.

Earlier studies showed that electrode materials are derived from covalent organic frameworks with isolated active sites. These materials usually show lower specific capacities [10]. For instance, a two-dimensional COF called 2D CCP-HATN was reported by Xu et al. It has one redox-active C=N group and sp^2-carbon bonds. Its theoretical capacity is limited to 117 mAh/g [11]. Electrodes derived from covalent organic frameworks featuring multiple redox-active centers typically achieve higher specific capacities. BQ1-COF is a new two-dimensional COF that was reported by Wu et al. It contains a lot of C=O and C=N redox-active groups. Because BQ1-COF contains several redox-active centers, it boasts a substantial theoretical capacity of 773 mAh/g [12]. Yang et al. synthesized a COF-TRO material featuring high-density C=O active sites designed for application as cathodes in lithium-ion batteries (LIBs). Electrochemical tests and theoretical calculations demonstrated that each COF-TRO unit can accommodate six lithium ions, enabling significant lithium storage. After completing 100 cycles at a 0.1 C current rate, the discharge capacity reached 268 $mAh \cdot g^{-1}$. This capacity is nearly comparable to the theoretical capacity of 274 $mAh \cdot g^{-1}$. These results indicate that COF-TRO exhibits excellent utilization of active sites [13].

Liu and colleagues recently introduced USTB-6. It is a crystalline covalent organic framework with dual porosity. This COF was created by polymerizing redox-active components. These components contain a high number of carbonyl (C=O) and imine (C=N) groups. Through graphene-directed heterogeneous polymerization, graphene-loaded COF nanosheets (USTB-6@G) were created, greatly increasing the COF-based electrode's electrical conductivity. At a current density of 0.2 C, the USTB-6@G cathode demonstrated a high specific capacity of 285 mAh/g and maintained an outstanding rate performance of 188 mAh/g at 10 °C. Notably, after 6000 cycles at 5 C, the USTB-6@G cathode maintained a capacity of 170 mAh/g, demonstrating exceptional cycling stability. Due to its high capacity and long-cycle stability, USTB-6@G is positioned as one of the best COF-based electrodes for LIBs [14]. By integrating multi-walled carbon nanotubes (CNTs) into the DAPQ-COF framework, Gao et al. created a novel two-dimensional β-ketoenamine-linked composite covalent organic framework (DAPQ-COFX). There are a lot of accessible C=O groups in the composite. Under a current density of 500 mA/g, the DAPQ-COF50 variant's maximum capacity was 162 mAh/g. This performance is equivalent to 95% of redox-active sites being used [15].

Conjugated systems capable of forming conjugated π-bonds typically feature a sequence of single and double bonds. Enhancing the electrical conductivity of COFs can be achieved by synthesizing highly conjugated structures. In order to create a high-conductivity cathode material for lithium-ion batteries (LIBs), Huang et al. created a highly conjugated TFPPy-ICTO-COF connected with olefins. 1.0×10^{-3} S cm^{-1}. The material has several active sites thanks to the many C=O groups. Under an applied current density of 0.1 $A \cdot g^{-1}$, the TFPPy-ICTO-COF electrode demonstrated an exceptional capacity of 338 $mAh \cdot g^{-1}$ and, after 11,000 cycles, retained a reversible capacity exceeding 200 mAh/g [16].

4. COFs as anode materials in LIBs

In 1991, graphite anodes were introduced to the market for lithium-ion battery applications. Graphite is now the most often utilized anode material in commercial lithium-ion batteries because of its inexpensive cost, minimum volume expansion (10%), low working potential (0.1 V), and layered structure. Nevertheless, the relatively modest theoretical capacity of 372 $mAh\cdot g^{-1}$ for graphite anodes significantly hampers the escalating demand for high-energy-density lithium-ion batteries. This restriction limits lithium-ion batteries' electrochemical performance [17]. Consequently, substantial efforts have been directed toward developing novel anode materials with ultra-high capacities to replace graphite. COFs are recognized as highly promising candidates for anode applications in lithium-ion batteries, attracting extensive research interest due to their multiple advantages. For instance, COFs possess high BET surface areas and high porosity, which facilitate efficient lithium-ion transport. Additionally, COFs can be functionalized with targeted functional groups to enhance interactions with lithium ions, thereby improving battery performance. Moreover, COFs exhibit excellent cycling stability and rate capability, making them strong candidates for high-performance lithium-ion battery anodes. Like COF-based cathode materials, strategies to improve COF anode performance focus on adding a large number of redox-active sites, making composites with conductive additives, and exfoliating COF layers to shorten ion diffusion paths and to prevent layer restacking. Adding many redox sites aims to increase the theoretical capacity and to provide multiple accessible redox potentials per unit mass. Making composites with conductive additives, for example carbon nanotubes or graphene, aims to form continuous electron pathways and to raise electronic conductivity without blocking pores. Exfoliating bulk COFs into thinner sheets reduces ion transport distances, exposes more active sites, and helps maintain structural stability during cycling. During charging, uneven deposition of alkali metals can cause dendrite growth, and these dendrites can damage the electrode and the separator and so shorten battery life. This issue is a primary reason why high-energy-density metal monomers cannot be directly used as anodes in alkali metal ion batteries. Currently, the most common anode materials include commercial graphite, commercial hard carbon, and hard carbon synthesized with biomass carbon templates. While graphite can somewhat limit dendrite formation and improve cycling performance, its theoretical capacity is significantly lower than that of alkali metal monomers. Most COF materials possess two-dimensional structures akin to graphite layers. However, low conductivity, long channels, and large pore volumes are the results of extensive π-π interactions between layers. It becomes challenging for ions and electrons to reach deeply entrenched active sites as a result of the delayed ion and electron transit caused by this. In order to stabilize anode materials, research on COF anodes thus mainly concentrates on designing a large number of redox-active sites, improving conductivity, developing electrode coatings, and exfoliating COFs.

Xu et al. Synthesized Tp-Azo-COF with a flower-like morphology through a solvothermal reaction between 4,4′-azodiphenylamine (Azo) and 1,3,5-tricarbonylresorcinol (Tp). This COF was integrated into lithium-ion half-cells and assessed for its electrochemical properties. The Tp-Azo-COF exhibited exceptional prolonged cycling stability, maintaining a substantial capacity of 305 mAh/g after 3,000 cycles with minimal capacity degradation. This performance highlights the promising application of Tp-Azo-COF in lithium-ion batteries [18, 19]. Zhao et al. reported Tp−Ta-COF. This COF was modified to contain two types of active centers, and it includes both C=N and C=O functional groups. Under an elevated current density of 2 $A\cdot g^{-1}$, Tp−Ta COF delivered a specific capacity of 195 $mAh\cdot g^{-1}$, demonstrating favorable rate capability and rapid charge–discharge kinetics, demonstrating stable cycling performance under the reported conditions [20].

Conjugated systems can form conjugated π-bonds and typically exhibit alternating single and double bonds. In electrode materials, designing highly conjugated COFs effectively enhances electrical conductivity. Bai et al. synthesized two fully conjugated materials, N2-COF and N3-COF, using a solvothermal method. These COFs achieved large specific surface areas of 1496 m^2/g and 1142 m^2/g, respectively, surpassing graphene's 600–700 m^2/g. They were produced from 1,3,5-tricarbonylbenzene and two amine derivatives through aldehyde and ammonia condensation reactions. Operating at a current density of 1 A/g, N2-COF and N3-COF demonstrated initial discharge capacities of 735 mAh/g and 731 mAh/g, respectively. After 500 cycles, their capacity retention rates remained at 82% and 83%, respectively, highlighting their outstanding cycling stability. Upon returning to 0.2 A/g, capacities returned to initial levels, demonstrating superior adaptability to high currents and robust performance [21]. These properties result from the high conductivity due to the fully conjugated structure, marking the first application of fully conjugated COFs in lithium-ion batteries.

Li et al. introduced an imine-functionalized two-dimensional mesoporous COF named TFPB-COF, fabricated via a Schiff base condensation reaction. TFPB-COF was chemically exfoliated using $HClO_4$, resulting in E-TFPB-COF. Additionally, incorporating MnO_2 nanoparticles into E-TFPB-COF effectively prevented re-stacking during charge and discharge cycles. Compared to the bulk TFPB-COF, exfoliation generated additional lithium incorporation sites associated with delocalized aromatic π-electron systems, thereby enhancing ionic and electronic transport dynamics; after 300 cycles, E-TFPB-COF/MnO_2 and E-TFPB-COF retained reversible capacities of 1359 mAh g^{-1} and 968 mAh g^{-1}, respectively [22]. The electrodes demonstrated excellent high-rate capability and sustained capacity maintenance under elevated current densities. This behavior supports their application in high-power lithium-ion batteries.

5. Conclusion

Because of their large surface areas, tunable pore structures, structural stability, and high designability, COFs have become a promising material for lithium-ion battery (LIB) electrodes. The substantial progress in using COFs as cathode and anode materials for LIBs has been emphasized in this review. Through techniques like adding conductive additives and creating highly conjugated structures, COF-based cathodes gain increased conductivity and multiple redox-active sites, which improves their reversible capacities and cycling stability. Comparably, COF anodes outperform conventional graphite anodes in terms of capacity by utilizing their porous structures and functionalized groups to enable effective lithium-ion transport and multi-electron storage.

Although progress has been made, several challenges remain. Many covalent organic frameworks (COFs) exhibit naturally low electrical conductivity, and the limited theoretical capacity of individual active sites restricts their practical application. To solve these problems, researchers pursue several complementary strategies. First, they increase the density and the chemical diversity of redox-active centers by introducing multiple types of redox groups and by raising site concentration. Second, they improve electronic transport by extending π-conjugated backbones to enlarge electronic delocalization and to lower charge-transfer barriers. Third, they form composites with conductive materials so that continuous electron pathways are established and charge transport is improved.

Future research should focus on solving scale-up and reproducibility problems in COF synthesis. It should also improve inherent conductivity without reducing pore volume, and ensure electrolyte compatibility and stable interfaces. Researchers need to develop scalable synthesis routes that give consistent batches, and they should test processing methods that add conductive pathways while preserving porosity. They should also examine chemical and electrochemical compatibility with common electrolytes, and study how electrode–electrolyte interfaces form and change during cycling. To advance COF-based electrodes from lab research to applications in large-scale energy storage, portable electronics, and electric cars, these issues must be resolved.

References

[1] Manthiram A. An outlook on lithium-ion battery technology. ACS central science, 2017, 3(10): 1063-1069.

[2] Wang T, Kailasam K, Xiao P, et al. Adsorption removal of organic dyes on covalent triazine framework (CTF). Microporous and Mesoporous Materials, 2014, 187: 63-70.

[3] Kuhn P, Antonietti M, Thomas A. Porous, covalent triazine-based frameworks prepared by ionothermal synthesis. Angewandte Chemie International Edition, 2008, 47(18): 3450-3453.

[4] Zhao Q, Zhu Z, Chen J. Molecular engineering with organic carbonyl electrode materials for advanced stationary and redox flow rechargeable batteries. Advanced Materials, 2017, 29(48): 1607007.

[5] Kim K C, Liu T, Lee S W, et al. First-principles density functional theory modeling of Li binding: thermodynamics and redox properties of quinone derivatives for lithium-ion batteries. Journal of the American Chemical Society, 2016, 138(7): 2374-2382.

[6] Song Z, Zhou H. Towards sustainable and versatile energy storage devices: an overview of organic electrode materials. Energy & Environmental Science, 2013, 6(8): 2280-2301.

[7] Zhang C, Lu C, Zhang F, et al. Two-dimensional organic cathode materials for alkali-metal-ion batteries. Journal of energy chemistry, 2018, 27(1): 86-98.

[8] Xu Z, Rahman M M, Mu L, et al. Chemomechanical behaviors of layered cathode materials in alkali metal ion batteries. Journal of Materials Chemistry A, 2018, 6(44): 21859-21884.

[9] Sun J, Xu Y, Lv Y, et al. Recent advances in covalent organic framework electrode materials for alkali metal-ion batteries. CCS Chemistry, 2023, 5(6): 1259-1276.

[10] Wang S, Wang Q, Shao P, et al. Exfoliation of covalent organic frameworks into few-layer redox-active nanosheets as cathode materials for lithium-ion batteries. Journal of the American Chemical Society, 2017, 139(12): 4258-4261.

[11] Xu S, Wang G, Biswal B P, et al. A nitrogen-rich 2D sp2-carbon-linked conjugated polymer framework as a high-performance cathode for lithium-ion batteries. Angewandte Chemie, 2019, 131(3): 859-863.

[12] Wu M, Zhao Y, Sun B, et al. A 2D covalent organic framework as a high-performance cathode material for lithium-ion batteries. Nano Energy, 2020, 70: 104498.

[13] Yang X, Hu Y, Dunlap N, et al. A truxenone-based covalent organic framework as an all-solid-state lithium-ion battery cathode with high capacity. Angewandte Chemie International Edition, 2020, 59(46): 20385-20389.

[14] Liu X, Jin Y, Wang H, et al. In situ growth of covalent organic framework nanosheets on graphene as the cathode for long-life high-capacity lithium-ion batteries. Advanced Materials, 2022, 34(37): 2203605.

[15] Gao H, Zhu Q, Neale A R, et al. Integrated covalent organic framework/carbon nanotube composite as Li-ion positive electrode with ultra-high-rate performance. Advanced Energy Materials, 2021, 11(39): 2101880.

[16] Xu X, Zhang S, Xu K, et al. Janus dione-based conjugated covalent organic frameworks with high conductivity as superior cathode materials. Journal of the American Chemical Society, 2022, 145(2): 1022-1030.

[17] Xie J, Lu Y C. A retrospective on lithium-ion batteries. Nature communications, 2020, 11(1): 2499.

[18] Zhao H, Chen H, Xu C, et al. Charge storage mechanism of an anthraquinone-derived porous covalent organic framework with multiredox sites as anode material for lithium-ion battery. ACS Applied Energy Materials, 2021, 4(10): 11377-11385.

[19] Cui S, Miao W, Peng H, et al. Covalent Organic Frameworks as Electrode Materials for Alkali Metal-ion Batteries. Chemistry–A European Journal, 2024, 30(12): e202303320.

[20] Zhao G, Sun Y, Yang Y, et al. Molecular engineering regulation redox-dual-active-center covalent organic frameworks-based anode for high-performance Li storage. EcoMat, 2022, 4(6): e12221.

[21] Yang X, Gong L, Wang K, et al. Ionothermal synthesis of fully conjugated covalent organic frameworks for high-capacity and ultrastable potassium-ion batteries. Advanced Materials, 2022, 34(50): 2207245.

[22] Chen X, Li Y, Wang L, et al. High-lithium-affinity chemically exfoliated 2D covalent organic frameworks. Advanced Materials, 2019, 31(29): 1901640.