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Perspective

Covalent organic frameworks: a new platform for next-generation batteries of Na-, K- and Zn-ions

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With the rapid development of globalization and growing energy consumption, there is a huge demand for smart grids, electric vehicles, and large-scale energy storage. Hundreds of electrochemical energy storage devices with high efficiency have been developed and explored. In recent years, lithium-based batteries have been widely developed and achieved groundbreaking progress in practical applications, which are accepted as an effective way to realize high-energy-density electronic devices [1]. However, it is undeniable that lithium-based batteries have entered a bottleneck period, and many technical problems need to be solved urgently. The energy density can hardly be improved, as the traditional lithium batteries with Li-C anodes are close to the maximum theoretical capacity (370 mA g^{-1}) [2]. Although lithium-sulfur (Li-S) batteries have been developed as an alternative to achieve higher theoretical capacity, pure lithium anodes are required to realize high energy density, and the safety issues, such as thermal runaway caused by lithium metal, cannot be ignored and are intractable. In addition, the "shuttle effect" caused by polysulfides results into relatively poor stability [2]. On the other hand, the sustainability and the limited availability of lithium reserves result in higher cost of lithium-based batteries, and the huge challenges in fast charging and adapting to temperature ranges hinder the larger-scale deployment applications (electric vehicles, energy storage) [3]. Therefore, researchers have been looking for a new secondary battery technology to make up for the insufficiency of lithium batteries. In this case, enormous efforts have been made on alternative energy storage technologies such as sodium (Na), zinc (Zn), and potassium (K) battery systems, owing to the relatively lower cost, higher earth abundance and characteristics similar to Li-based batteries.

As the key components of batteries, electrodes, electrolytes, and separators have closely effect on the electrochemical performance of energy storage devices. A battery system with multifunctional and highly active materials can ensure the efficient charging and discharging process, and achieve the goal of efficient energy storage and conversion. Therefore, developing novel functional materials for advanced Na-, K-, Zn-based batteries is the key to alleviating the current energy crisis, innovating traditional power grids, and building a new generation of the integrated energy systems. In the early research period, researchers' attention was mainly focused on inorganic materials and amorphous polymeric materials, which are extensively applied in the above-mentioned new batteries, and some progress has been made [4]. However, the current electrochemical indicators, such as the stability of these batteries, still cannot meet the need for industrial applications. Ideal electrochemical materials for Na/Zn/K-based batteries require the following characteristics: stable structures, good physical and chemical stability, high ionic diffusion coefficient, high electrical conductivity, abundant resources, and facile synthesis. At present, no materials can meet all these characteristics. Therefore, it is still greatly challenging to develop and evaluate new functional materials that meet all of the critical requirements of high specific capacity, high energy density, long lifespan, and affordable price [5]. Compared with organic materials, covalent-organic frameworks (COFs) which are constructed by lightweight elements such as C, H, N, O, B and connected by covalent bonds are an emerging class of new functional materials. Since their discovery, COFs have attracted a lot of attention in electrocatalysts, photovoltaics, field-effect transistors, light-emitting diodes, selective transport, sensors, and drug delivery systems [6]. Recently, COFs have emerged in Na-, Zn-, and K-ion batteries as functional materials (Fig. 1). There are several advantages of COFs (Fig. 2): (1) due to the diversity of building monomers and synthetic methods, active functional groups or benign ionic conductors can be introduced into COF channels, which realizes the directional modification of pores; (2) the well-defined channels could be regarded as the efficient pathways to boost the ion transportation, reduce the energy barrier of ion diffusion and enhance ionic conductivity; (3) benefiting from the components of lightweight elements such as C, H, N, O, B, batteries constructed by COFs deliver a high energy and power density; (4) with covalent bond connection and π-π conjugated structures, COFs often show an excellent stability and are heterogeneous in most organic solvents; COFs exhibit an unique mechanism of the ion-transfer which are obviously different from the traditional inorganic and polymer materials, and could be promising candidates for every component in the Na-, Zn-, and K-ion batteries (electrode, electrolyte and separator).

COFs as electrodes. Initially, COFs are most commonly used as advanced electrodes (cathode and anode materials) in the next-generation lithium-based batteries to provide reversible capacity, due to the high porosity, redox-active sites, and regular channels

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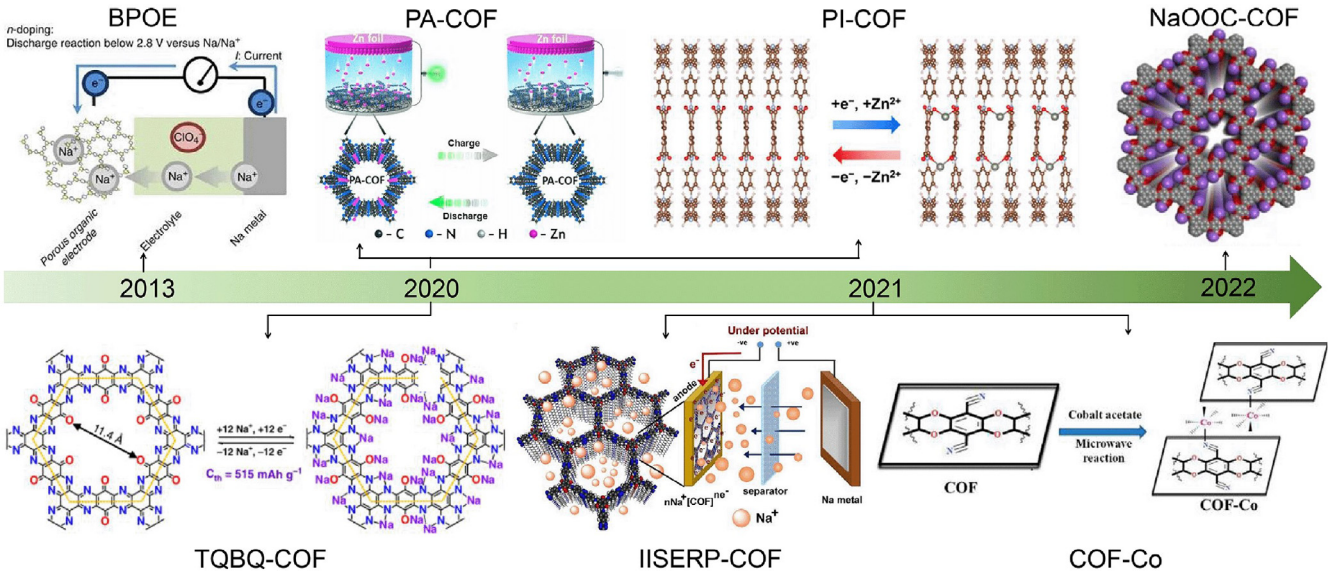

Fig. 1. (Color online) The timeline of COFs (BPOE [7], TQBO-COF [8], PA-COF [9], IISERP-COF [10], PI-COF [11], COF-Co [12], and NaOOC-COF [13]) as electroactive materials in Na-, Zn-, and K-ion batteries.

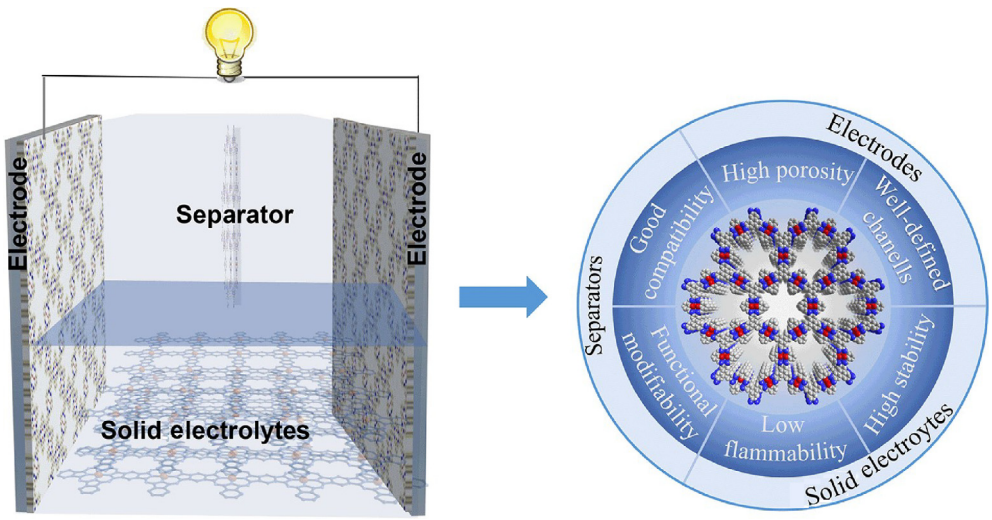

Fig. 2. (Color online) Schematic illustration showing rechargeable batteries with COFs as functional materials and the advantages of covalent organic frameworks as electrodes, solid electrolytes, and functional materials for next-generation rechargeable batteries.

[4]. Microporous (1.4 nm) bipolar COFs with active triazine rings and inactive benzene rings in the skeletons were reported as the cathode of Na-ion batteries, showing specific capacities of ~200 and 10 mAh g^{-1} at 0.01 and 10 A g^{-1} [7]. For the honeycomb-like TQBQ-COF, with pyrazines and carbonyls as redox sites, its energy gap was effectively reduced and the conductivity was enhanced. Moreover, using as the cathode of Na-ion batteries, it exhibits a high capacity of 452.0 mAh g^{-1} at 0.02 A g^{-1} and a high-rate capability of 134.3 mAh g^{-1} at 10.0 A g^{-1} [8]. Recently, a phenanthroline based covalent-organic framework (PA-COF) [9] was developed and used as the cathode material for an aqueous Zn-ion super-battery, demonstrating a high capacity of 247 mAh g^{-1} at a current density of 0.1 A g^{-1} and an average capacity decay of only 0.38% per cycle during 10 000 cycles at a current density of 1.0 A g^{-1}, and opening a new direction for COF electrodes in aqueous ion batteries. In addition, three large mesoporous COFs with active phenyl (IISERP-COF16), tetrazine (IISERP-COF17) and bispyridine-tetrazine (IISERP-COF18) rings in the skeletons reported by Vaidhyanathan's group [10] was developed as anodes of the Na-ion battery, and yielded a high specific capacity of 340 mAh g^{-1} @1 A g^{-1} and an excellent cycling stability with 92% capacity retention even up to 1400 cycles. A two-dimensional polyarylimide covalent organic framework (PI-COF) [11] with well-organized pore channels was also reported as the anode of Zn-ion batteries. Benefiting from the high accessibility of the build-in redox-active carbonyl groups and efficient ion diffusion with a low energy barrier, it exhibited high specific capacity (332 C g^{-1} or 92 mAh g^{-1} at 0.7 A g^{-1}), high-rate capability (79.8% at 7 A g^{-1}), and a long cycle life (85% over 4000 cycles). A dendrite-free full Zn-ion device fabricated by coupling PI-COF anode with MnO_2 cathode demonstrated an excellent energy density (23.9–66.5 Wh kg^{-1}) and a supercapacitor-level power density (133–4782 W kg^{-1}). Moreover, by introducing Co centers into the cyano-COF via a facile microwave digestion reaction, COF-Co was synthesized and acted as an anode material for K-ion batteries [12]. The introduction of Co active sites provided enhanced π-π stacking, more defects, and

enlarged layered distance for the two-dimensional COF structure, which improved K^+ insertion/extraction kinetics behaviors and led to a high reversible potassium storage capacity (371 mAh g^{-1} after 400 cycles of 0.1 A g^{-1}) in K-ion batteries.

COFs as solid electrolytes. Taking advantages of low flammability, high thermal stability, no leakage, and low explosion hazard, solid-state electrolyte is a new technology with great potential for improving battery performance significantly, which attracts wide attention in both academia and industry fields [14]. More importantly, the solid electrolyte can effectively suppress the growth of metal dendrites due to its excellent mechanical strength, which is beneficial to obtain higher energy and power density. Notably, COFs are also promising and optimal platforms for solid-state ion conductors due to their precisely oriented and well-defined ion channels. Up to date, there are very few reports on COFs as solid electrolytes for Na-, Zn-, and K-ion batteries, and research of COFs as electrolytes is still in the initial stage. The first example reported by Guo's group [13] is a carboxylic acid sodium functionalized polyarylether linked COF (NaOOC-COF), which was developed as an advanced Na-ion quasi-solid-state conductor film. Benefiting from the well-defined ion channels, NaOOC-COF achieved an exceptional Na^+ conductivity (2.68×10^{-4} S cm^{-1}) with only 0.24 eV activation energy (E_a) and a high transference number of 0.9. Moreover, NaOOC-COF delivered a good long-time cycling performance in the assembled quasi-solid-state battery. The dendrite growth also can be suppressed by interface regulation. This study not only contributes to a new solid-state electrolyte and Na metal battery for sustainable and inexpensive energy storage system, but also accelerates the progress of functionalized COFs, which are increasingly in demand for high-performance solid-state ion conductors.

COFs as functional separators. As a unique component of Na-, Zn- or K-ion based batteries, functional separators can effectively suppress the loss of active materials and the growth of metal dendrites, endow a more stable electrode/electrolyte interphase, and improve the safety and conform a high energy density of the battery systems [6]. Taking advantage of good stability of structure and compatibility with the organic electrolytes, COFs are regarded as a promising candidate for functional separators for Na-, Zn- or K-ion-based batteries. Unfortunately, there are no reports on COFs as separator modification materials for Na-, Zn- or K-ion batteries, limited by the difficulty in preparing COFs films with an appropriate mechanical strength, regular pore structures, and good compatibility. Therefore, COFs as functional separators in Na-, Zn-, and K-ion batteries are considered as a huge challenge.

Although certain progress has been made, COFs-based functional materials for Na-, Zn-, and K-ion batteries are still limited by some technical issues. Firstly, to address potential safety risks of batteries, COFs should possess excellent structural and chemical stability. Secondly, good electronic and ionic conductivities are strong guarantees for the storage properties of Na, Zn and K, ensuring a promising specific capacity and rate performance. Thirdly, active sites can adjust the electrochemical micro-environment at the electronic level, confirm the electrochemical efficiency during the charge/discharge process, and provide a clear molecular platform to clarify the mechanism. Lastly, COFs nanosheets or nanotubes can effectively facilitate charge separation and transfer to guarantee high efficiency. The detailed perspective can be expanded on the following aspects:

(1) To improve the stability. An excellent structural and chemical stability in organic electrolytes and a certain voltage range are the primary requirements for COFs acting as electrodes, solid electrolytes, or functional materials of modified separators in the battery systems. Most traditional COF materials are mainly composed of C=N, C–N, or B–O bonds, which are normally unstable and would lead to the disintegration of the COF skeleton structure in organic solvent with strong polar molecules, strong acids, or alkaline solution and other harsh chemical environments. Recently, nitrogen-containing hydrazone- and azine-linked COFs have been explored and exhibited higher chemical stability than imine-functionalized COFs. Strong covalent bonds and full π-π conjugation interactions have been considered as effective ways to exploit innovative COFs that are emerging as promising candidates for Na-, K-, Zn-ion functional materials.

(2) To improve the conductivity. Limited by the conductivity, electroactive COFs are still needed to be improved. COF-based derivatives obtained by carbonization under a high temperature can deal with this problem. However, it is often uncontrollable, and the unique structural integrity of COF materials cannot be preserved. Recently, introducing electroactive building blocks or incorporating conductive components into COFs is considered as an effective alternative solution. The most important strategy is the development of COFs with intrinsically highly conductivity. Specially, structures with crystalline and ordered channels are essential for electron or ion conductivity. Besides, the interactions between layers and extended π-conjugated skeletons also have a positive effect on the conductivity of COFs. For the general design, the interlayer distances would be shortened and provide a highly efficient electronic transition pathway. Constructing COFs with high conductivity by tuning the unique π-conjugation structure has been considered as an effective way to boost electroactivity, and is expected to realize the discovery of new functionalized electrodes for Na-, K- and Zn-ion batteries.

(3) To construct more active sites. Due to the lack of highly active metal catalytic centers in COFs, electrons cannot be efficiently utilized, which greatly limits the electrochemical activities of COFs. Besides, it is difficult to further optimize the active sites by regulating the electronic structure, which greatly limits the conductivity, capacity, and energy densities. In view of these disadvantages, the redox/catalytic active sites, such as heteroatoms (N, O, S, B) or metal atoms, can be pre-introduced by the construction of benzoxazole and phenazine-linked skeleton or accurately anchored to specific sites on the COF backbones with the predesigned environment. Hence, the electronic structures can be purposefully tuned, offering great opportunities for tailoring the electroactivity and making COFs as platforms for the mechanism and structure–function relationship study. It is worth noting that, metal nanoclusters with abundant active metal centers could be stably loaded on COF carriers by electrostatic interaction or covalent bonding, demonstrating excellent prospects for electrochemical applications. This is also an ideal tactic for the preparation of highly active and stable composite materials.

(4) To treat with special nanostructures. Defects and boundaries caused by the bulk COFs particles tend to hinder charge migration and transportation. In addition, the long channels of COFs formed by stacked layers also cause a great hindrance for electrons or charge diffusion to the active sites, which limits the wide-range applications. To overcome these obstacles, COFs could be assembled into some specific nanostructures, such as π-conjugated nanosheets or nanotubes with a thickness of single or few atomic layers. The large number of isolated reaction sites could contribute to improving charge separation and carrier efficiency, therefore effectively improving the electrical activity. This means that the transport pathways of ions to the active sites can be effectively shortened and a sufficient electron conduction path from the electrode to the active sites can be provided. COFs nanosheets or nanotubes with tunable electronic properties and fully exposed active sites would have unique properties for the application in Na-, K- and Zn-ion batteries. In addition, π-conjugated nanosheets or nanotubes have special advantages on the preparation of solid electrolytes and separator functional materials, which are beneficial to the preparation of micro-nano battery devices beyond lithium with high power density and volumetric energy density.

In conclusion, it remains tremendous challenges for the application of COFs as electroactive materials in the new generation rechargeable batteries based on Na-, Zn- and K-ions. According to different requirements for components in batteries, more unique and novel structures need to be explored, and great efforts should be devoted to building the structure–function relationship. This perspective analyzes the challenges faced by COFs as different roles in the new generation rechargeable batteries in detail and puts forward several constructive suggestions, which would be helpful in the understanding of the mechanism of COFs as different components of batteries. Also, it provides theoretical guidance for future research on COFs-based functional materials for Na-, Zn-, and K-ion batteries and emphasizes the importance of battery design guided by the structure–activity relationship.

Conflict of interest

The authors declare that they have no conflict of interest.

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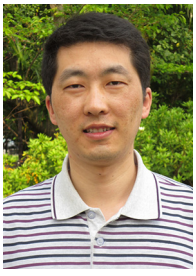

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