Covalent Organic Frameworks Solid-State Electrolytes

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Covalent organic frameworks (COFs) have emerged as a promising platform of materials for solid-state battery electrolytes due to their porous and robust structures, and their special spaces such as 1D and 3D, as well as their ability to be modified with functional groups.

electrolytes covalent organic frameworks (COFs)

1. Covalent Organic Frameworks Solid-State Electrolytes

The electrolyte plays a crucial role in solid-state batteries (SSBs). Extensive research has been conducted by scientists to identify optimal building blocks, preparation routes, and functional groups for covalent organic frameworks (COFs) as potential electrolyte materials ^[1]. Among other methods, COFs can be categorized based on the types of chemical bonds present within their structures. These include B-O bonds, such as boronate ester, boroxine, borosilicate, and spiroborate; C-N bonds, including imine, imide, hydrazone, amide, β-ketoenamine, azine, phenazine, squaraine, viologen, triazine, and melamine; C-C bonds; borazine (B-N) bonds; and azodioxide (N-N) bonds ^[1]. Each type of chemical bonds imparts unique properties to a COF, influencing its overall performance as an electrolyte material.

2. C-N Linkage

Among the various types of COFs, those containing nitrogen bonds have garnered significant attention due to their distinct properties and potential benefits in electrolyte applications. Nitrogen atoms can participate in chemical bonding, forming diverse linkages such as imine, hydrazone, amide, and triazine. The inclusion of nitrogen atoms within the COF structure introduces several advantages. A key advantage of nitrogen-containing COFs is their facilitation of ion transport. The presence of nitrogen atoms enhances the coordination and migration of ions within the material, resulting in improved ionic conductivity. This property is crucial for efficient ion transport in solid-state electrolytes, enabling faster charge and discharge rates in batteries. Moreover, nitrogen-based COFs exhibit exceptional stability and chemical inertness, which are vital for ensuring the reliable and safe operation of batteries. The incorporation of nitrogen atoms enhances the structural integrity and thermal stability of COFs, enabling them to withstand harsh operating conditions.

2.1. Imine Bond

The imine type of bond has received significant attention in the literature. An imine linkage is known for its stability and ease of formation between primary amine and C_3 -symmetric trialdehyde benzene and its derivatives. Nitrogen, with its available electron pair, serves as a donor and is particularly useful for stabilizing cations such as Li⁺, Na⁺, and others. Imine groups act as a chromophore group and products typically range in color from yellow to red. Additionally, the presence of imine groups imparts chromophoric properties to the COFs, resulting in a range of colors from yellow to red because of the extension of conjugation along the double bonds of imine bonds (C=N) of their products. These examples highlight the versatility and potential of imine-based COFs in various fields, including electrolytes.

The simplest building blocks used in COFs are 1,3,5-triformylbenzene (TB) and 1,4-diaminobenzene (TP). Xu et al. ^[2] investigated a COF material derived from TB and TP. In their study, the authors addressed the issue of lithium dendrite growth during lithium plating on the anode when using a typical liquid electrolyte. In batteries cycled with a standard liquid electrolyte, a protective solid electrolyte interphase (SEI) is formed. However, under high-current charging, the SEI can decompose, leading to the growth of dendritic lithium crystals through the electrolyte. To address this issue, the authors proposed an artificial "SEI" in their study ^[2]. They coated a copper current collector with TB-TP soaked in LiTFSI using spin coating and performed lithium plating between the copper and COF. Subsequently, the authors conducted stripping/plating cycling experiments. The results showed no formation of lithium dendrites and a dense and uniform layer of lithium. The authors reported a transference number of 0.85, as compared to 0.35 for 1 M LiTFSI in DOL/DME, indicating that this material could effectively function as an electrolyte.

2.2. Imide Bond

One of the other described C-N systems is the imide bond. Polyimide polymers are well known for their good thermal stability, chemical resistance, and great mechanical properties. Imide bond-linked COFs are formed from the condensation reaction of aromatic anhydride and C_3 -symmetric aromatic primary amine through the formation of aromatic amic acid as an intermediate, and depending on the substrate structure, the formed COFs have hexagonal, square, or triangular shape pores.

Imide bonds have significant thermal stability which was shown in the publication from Wang et al. ^[3]. Their COFbased material was constructed with pyromellitic dianhydride (PMDA) and 2,4,6-tris(2-aminophenol)-1,3,5-triazine (TAPOA) at 180 °C for 5 days in the presence of isoquinoline as a catalyst in a mesitylene/NMP mixed solution. The obtained material, denoted as NKCOF-11, showed imide bonding and high crystallinity. The authors conducted an in-depth study on the behavior of NKCOF-11 at high temperatures. Up to around 350 °C, the basic structure remained unchanged, but a thermally induced structural rearrangement from the imide- to the benzoxazole-linked COF (named TR-NKCOF-11) occurred around 400 °C, and more carbonization occurred above 650 °C. Compared to other COF-based materials (boronate ester, imine, imide, β -ketoenamine, and olefin, details in ^[3]), NKCOF-11 showed remarkable resistance with respect to a fire test. In order to enhance conductivity, PEG chains and LiTFSI salt were incorporated into the pores of both samples. NKCOF-11 showed good Li-ion conductivity specified as 1.36 × 10⁻⁵ S·cm⁻¹ at 30 °C, low energy activation of 0.18 eV, with almost pure ionic conductivity (the transference number was 0.95). TR-NKCOF-11 prepared in the same way showed a lower conductivity value specified as 2.24 $\times 10^{-6}$ S·cm⁻¹ at 30 °C. It is worth mentioning that NKCOF-11 represented impressive electrochemical stability up to 5.5 V vs. Li|Li⁺, which was compatible with state-of-the-art cathode materials like LiNiPO₄ olivine ^[4].

2.3. β-Ketoenamine Bond

Jeong at al. proposed an interesting method of increasing ionic conductivity in a β -ketoenamine COF system ^[5]. Aa a standard method of preparation, the COF as SSEs contained both Li salt and solvent. The building blocks with cationic active centers dissolved Li salt without any solvent. The prepared COF was constructed with 1,3,5-triformylphloroglucinol (TP) and 1,4-phenylenediamine-2-sulfonic acid (Pa-SO₃H). TpPa-SO₃Li was obtained through ionic exchange using lithium acetate. TpPa-SO₃Li showed relatively small pores of 11.8 Å and a small surface area of 348 m² g⁻¹, with a conductivity of 2.7 × 10⁻⁵ S·cm⁻¹, a high transference number of 0.9, and low activation energy equal to 0.18 eV. TpPa-SO₃Li displayed excellent stability with the symmetrical Li cell Li|TpPa-SO₃Li|Li. The DFT calculations represented anisotropy in the conduction direction, low energy (7.6 kcal·mol⁻¹) in the axial pathway, and high energy in the planar direction (31.6 kcal·mol⁻¹).

2.4. Squaraine Linkage

A squaramide is one of the squaraine-type linkages that is composed of both zwitterionic and amide bonds via the condensation reaction of aromatic amines and squaric acid. Squaraines that contain squaramide exhibit appealing characteristics such as strong infrared absorption and photostability, which have been extensively described in previous studies ^{[S][Z]}. Wang et al. investigated the utilization of a squaraine-linked covalent organic framework (COF) as an additive for a polyethylene oxide (PEO)-based electrolyte ^[S]]. The COF, named HUT4, was synthesized by reacting melamine and squaric acid at 120 °C for 3 days. The resulting material exhibited a pore size of 15 Å and a surface area of 120 m² g⁻¹. They developed a hybrid electrolyte by embedding HUT4 in PEO and combining it with the lithium donor LiTFSI. Among the different compositions tested, the electrolyte with 10% HUT4 additive demonstrated the best performance, leading to good ionic conductivity of 8.2×10^{-6} S·cm⁻¹ at 30 °C, regardless of a moderate transference number of 0.62. This performance was nearly twice as good as that of the sample without the addition of HUT4. To further evaluate the applicability of this material, the authors assembled a S@CNT|PEO-10%HUT4|Li cell. Under operating conditions of 60 °C and a current rate of 0.2 C, the cell exhibited a capacity of approximately 1000 mAh g⁻¹, demonstrating the potential application of this material in Li-S batteries. Although this type of bonding has theoretically shown significant potential, it has not yet been properly explored.

The presence of ionic-type bonding in squaraine-type COF materials positions them as promising candidates for lithium-ion conductors. However, it is important to note that the strong electrostatic interactions between ions and structure raise the activation energy required for ion movement, potentially leading to reduced conductivity, as illustrated earlier. Nevertheless, their stable performance in Li-S batteries suggests that this material category holds significant potential and merits further comprehensive investigation.

2.5. Triazine Linkage

The triazine linkage is a chemical connection utilized in the construction of COFs that entail the bonding of nitrogen atoms within triazine rings. This linkage significantly contributes to the structural integrity and stability of the structure. Triazine-linked COFs have garnered significant interest, primarily owing to their remarkable thermal stability. Cheng et al. ^[9] presented an interesting example of a COF material with triazine-type bonds, which was synthesized by the condensation reaction of triazine and piperazine rings (NCS). The loose bonding between the triazine rings and cations reduced the energy barrier during ion transfer, which allowed for efficient movement of lithium ions. Additionally, the electrostatic forces with the piperazine rings acted as anchors, enhancing the selectivity of ion transfer by effectively binding anions. As a result, the NCS/electrolyte demonstrated exceptional room temperature lithium-ion conductivity, reaching up to $1.49 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$. This conductivity was achieved without the need for any solvent, only with the addition of LiTFSI, making it a promising and environmentally friendly option. Furthermore, the NCS/electrolyte exhibited a high transference number of 0.84, indicating efficient lithium-ion transport with minimal interference from other ions.

The example presented demonstrated a triazine-bonded material with significant promise as an electrolyte for solid-state batteries (SSB). This material exhibited high conductivity coupled with a favorable transference number. Its noteworthy characteristic of being devoid of oxygen contributed to enhanced thermal stability, although this aspect was not quantified in the study. However, further extensive research is warranted to explore the full potential of such materials.

3. C-B and O-B Linkages

In addition to the various types of chemical bonding found in covalent organic frameworks (COFs), carbon-boron (C-B) and oxygen-boron (O-B) linkages have emerged as noteworthy bonding motifs. COFs that incorporate C-B and O-B bonds have attracted considerable attention due to their unique properties and potential applications across diverse fields. The introduction of boron atoms into COF structures has brought about new functionalities and characteristics that could be tailored for specific purposes. COFs with oxygen-boron bonds, such as boronic acids and boroxinates, possess intriguing properties associated with their acidic nature and unique electronic structure. The presence of oxygen atoms in the boron-containing linkages facilitates proton transfer and acid–base interactions, rendering them potential candidates for proton-conducting materials, sensors, and drug delivery systems. Furthermore, the integration of oxygen-boron bonds within COFs imparts advantageous optical and electronic characteristics, thereby opening avenues for deployment in optoelectronic devices, photovoltaic systems, and as demonstrated in the following illustrative instances, as an electrolyte.

3.1. Spiroborate Bond

The spiroborate bond in COFs is a unique structural element where boron atoms form a closed ring with neighboring oxygen atoms, creating a stable and versatile linkage. This bond plays a crucial role in enhancing COF

stability and enabling various applications, particularly in the field of battery electrolytes, due to its excellent ionconducting properties. A good example is the works by Du et al. presented in ^[10].

All the COFs showed high crystalline two-dimensional structures ordered in A-A or A-B stacking. The boronate ester linkage contained sp3-hybridized boron which formed an ionic linkage. The presence of anionic boron centers in spiroborate-based COFs created possible routes for high conductivity paths. Therefore, the conductivities of ICOF-1 and ICOF-2 showed high porosities of 1022 m² g⁻¹ and 1259 m² g⁻¹, respectively, and they also possessed high thermal stability (mass loss up to 20% at 800 °C on TG measurement) and chemical stability vs. LiOH solution in water. Lithium ions were incorporated using LiOH (ICOF-2) instead of dimethyl amine base solution (ICOF-1) during COF formation. The conductivity of ICOF-2 was activated with an activation energy of 0.24 eV and moderate ionic conductivity of $3.05 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$ at room temperature. The transference number determined by the Bruce–Vincent–Evans method was 0.8. Among other properties, the high H₂ and CH₄ uptakes of ICOF-1 and ICOF-2 were of great worth as $3.11 \%_w$ at 77 K (1 bar) and $4.62 \%_w$ at 273 K (1 bar), respectively. Another advantage of the prepared materials was significant hydrolysis resistance. The authors' strategy of spiroborate formation provided the possibility of preparing porous materials with moderate electrolyte properties.

Other spiroborate COFs have also been reported by Zhang et al. ^[11], which were prepared from the reaction of γ -cyclodextrin and trimethyl borate with respective counter ions such as Li⁺, piperazine, and dimethyl amine (CD-COF-Li, CD-COF-PPZ, and CD-COF-DMA) using the microwave-assisted solvothermal synthesis method. The cyclodextrine-based COF presented a robust skeleton with a high specific area of 760 m²·g⁻¹. CD-COF-Li after loading with a standard liquid electrolyte (LiPF6 in EC/DEC) showed remarkable Li+ conductivity of 2.7 × 10⁻³ S·cm⁻¹ at 30 °C. The rapid Li⁺ transportation could be attributed to the flexible nature of γ -cyclodextrin also showed stable performance when cycling in a cell with symmetrical lithium metal electrodes. Interestingly, CD-COF-Li had high CO₂/N₂ sorption/desorption selectivity, which confirmed that this COF material was suitable for gas separation membranes.

The showcased examples demonstrate the potential of spiroborate-linked COF materials as viable electrolytes, attributed to their capacity for achieving high Li+ conductivity and impressive thermal stability. Moreover, the exceptional surface area of these materials opens up opportunities for their utilization in various other applications beyond electrolytes.

3.2. Boronate Ester

Boronic ester bonds, often referred to as boronate ester bonds, are a class of covalent bonds that involve boron atoms. These bonds are formed through the reaction between a boronic acid group and an alcohol group, resulting in the formation of a stable covalent linkage. Boronic ester bonds are highly valued in COF chemistry because of their reversible nature. They can undergo dynamic covalent chemistry, allowing for the disassembly and reassembly of COF structures under certain conditions. This reversibility makes boronic ester-linked COFs promising candidates for applications such as drug delivery systems, sensors, and molecular recognition, where controlled release or selective binding is required. In the realm of electrolyte applications, a paucity of research papers has explored the utilization of this specific bond type, with one notable exemplar presented below.

Vazquez-Molina et al. ^[12] described another interesting aspect of COF materials. In general, materials obtained by solvothermal reactions and other processes have polycrystalline aggregate structures. Chaotic crystal ordering leads to discontinuities in the optimal Li⁺ pathway, resulting in higher activation energies for Li⁺ transport and lower conductivity. The authors ordered the crystal grains of a boronate-bonded COF, described in the literature as COF-5, by applying uniaxial pressure. They used pressure in the range of 2–12 MPa, but the ordering of layers could be observed from 2 MPa, and a further increase in the pressure did not change the XRD pattern significantly. For the electrochemical measurements, the sample COF-5 was prepared by incorporating 1 M LiClO₄ in THF. The conductivity reached 2.6 × 10⁻⁴ S·cm⁻¹, but the authors did not specify the influence of the used pressure on the conductivity. The sample also presented extraordinary stability from –1 to 10 V vs. Li⁺|Li in the Li|LiClO₅@COF-5|cell setup. The high ionic conductivity, low temperature effect on conductivity, and high electrochemical stability makes crystallographically aligned COF-5 a competitive candidate for solid electrolytes in rechargeable Li-ion batteries.

The existing literature offers only a limited number of instances concerning boronate ester bonds in COFs. The provided example in ^[12] demonstrated a straightforward and efficient method for producing textured COF-5 with substantial conductivity. However, further comprehensive investigations are warranted to explore the full potential of these materials.

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