



Covalent organic frameworks with lithiophilic and sulfiphilic dual linkages for cooperative affinity to polysulfides in lithium-sulfur batteries



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ABSTRACT

Confining lithium polysulfides (PSs) within the cathode materials is one of effective solutions to improve cycling stability of lithium-sulfur batteries. The lithiophilicity and sulfiphilicity are two mainstreaming chemical interactions to stabilize lithium PSs, but they have been demonstrated independently in most of cathode materials with well-defined structures and chemical compositions. It is a great challenge for designing new materials to simultaneously elucidate such two types of chemical interactions at molecular level. Here, we develop a self-condensation approach of single building block to construct a covalent organic framework (COF) containing triazine and boroxine units (TB-COF). TB-COF was generated from 4-cyanophenylboronic acid through simultaneous formation of two types of reversible covalent bonds. The triazine unit chemically absorbs lithium ions through lithiophilic interaction, while boroxine unit traps PSs through sulfiphilic interaction. The amphiphilic chemisorption of lithium PSs has been elucidated by spectroscopic studies and theoretical calculations. The TB-COF/S electrode delivers a reversible capacity of 663 mA h g⁻¹ after 800 cycles at 1 C with the average capacity decay per cycle as low as 0.023%, which outperforms those in the reported COF-based sulfur cathodes.

1. Introduction

The ever-growing demand for energy consumption has driven the development of energy-storage technologies. Lithium-sulfur (Li-S) batteries have been regarded as one of the most promising electrochemical energy-storage systems due to their high theoretical energy density, low cost and environmental friendliness [1–3]. However, practical implementation of Li-S batteries has been impeded by several serious drawbacks. The major one is the dissolution and shuttle effect of lithium polysulfides (PSs), which are associated with fast capacity fading, low energy efficiency, severe self-discharge and poor cycling stability [4–6].

Tremendous efforts have been devoted to tailoring the nanostructure of carbon materials for improving the retention of active sulfur species within the sulfur electrodes. One of common methods is surface modification or heteroatom doping of carbon materials, in which PSs are synergetically confined in host materials by chemical interactions between porous matrix and PSs [7–10]. Generally, there are two types of mainstreaming chemical interactions to stabilize lithium PSs. One is lithiophilic interaction derived from heteroatom dopants or functional groups tethered on carbon materials [11–17]; the other is sulfiphilic

interaction, in which terminal sulfur atoms of PSs are trapped in topological defects/vacancies or bind to the exposed metal sites [18–20]. In the context, the reported sulfiphilic interaction is mostly based on inorganic solid materials with low specific surface area. Recently, carbon composite materials consisting of N-doped carbon and inorganic solid materials have been proposed to improve trapping efficiency and affinity of PSs, they have displayed promising electrochemical performances owing to synergetically lithiophilic and sulfiphilic interactions [17,21–24]. However, both functionalized carbon and inorganic solid materials have many types of surface sites, and the control over effective surface active sites is not practical, thus making it difficult to achieve sophisticated evidence to discern the interaction mechanism. In addition, the disordered porosities and non-uniform distribution of these functional groups have become major impediment to definitely elucidate underlying surface-binding mechanism of lithium PSs with host materials. Therefore, it is necessary to develop new materials with well-defined structure and periodic porous surface.

As one type of emerging crystalline porous materials, covalent organic frameworks (COFs) have received considerable attention owing to their large surface area, high stability and ready functionality [25–

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32]. Their structures and heteroatom components can be precisely controlled in principle through judicious selection of building blocks to optimize the desired functionality. These attributes make great opportunities to rationally design COFs as sulfur host materials for homogenous impregnation of sulfur species in their intrinsic pores [30–36]. The well-defined structures and chemical compositions provide an appealing platform to understand the chemical interactions between COF hosts and lithium PSs. For example, Wang and co-workers have reported triazine-based COFs [33] and imine-based COFs [34], which can trap PSs through lithiophilic interaction between nitrogen atoms and lithium ions. Tang and co-workers proposed one COF containing boroxine units [35], the positively polarized boron atoms and negatively polarized oxygen atoms can simultaneously adsorb PSs anions and lithium ions, thus greatly suppressing the shuttle effect of PSs. However, it is difficult to independently distinguish lithiophilic and sulfiphilic interactions of boron and oxygen atoms owing to their coexistence in boroxine units and cooperative adsorption toward PSs. Till now, COFs containing lithiophilic and sulfiphilic units have not been reported, which results in the lack of an ideal model for better understanding synergetic entrapping ability of lithium PSs.

The methodologies for design and synthesis of COFs have been well established in recent years, and a variety of functionalized COFs have been prepared through reversible condensation reactions, such as the formation of boronate, boroxine, imine, triazine, hydrazone and azine linkages [37–40], but most of COFs were assembled through one type of covalent bond formation reaction of different building blocks. In rare examples, binary COFs containing dual linkages [41,42] were prepared through orthogonal reaction strategy from two different building blocks. The binary COFs have integrated the physiochemical properties of two different linkages, and thus providing the chance to produce multifunctional materials. Despite the fascinating advantages of self-condensation reaction over orthogonal reaction, the synthesis of binary COFs through self-condensation approach of single building blocks has been unexplored hitherto. This is mainly attributed that simultaneous formation of two types of reversible covalent bonds is mutually interfered and even contradicted. Therefore, the construction of COFs containing dual linkages from single building blocks is an attractive but highly challenging task. Herein, we report one COF containing triazine and boroxine units (TB-COF), two types of linkages are simultaneously formed through self-condensation reaction of 4-cyanophenylboronic acid. The lithiophilic and sulfiphilic interactions between TB-COF and lithium PSs have been demonstrated owing to the coexistence of triazine and boroxine units, hence efficiently confining PSs within the cathodes and alleviating the shuttle effect of PSs, which are distinctly different from COFs containing single functional groups.

2. Experimental section

2.1. Synthesis of TB-COF

Trifluoromethanesulfonic acid (2 mL) was added dropwise to a solution of 4-cyanophenylboronic acid (0.5 g) in CHCl_3 (20 mL) at 0 °C in a 100 mL thick walled pressure bottle. The bottle was tightened by the screw cap and heated at 60 °C for 3 d. The precipitate was isolated by filtration and washed with copious CHCl_3 and acetone. The resultant material was further purified by Soxhlet extraction using acetone, dried in vacuo at 100 °C for 12 h to produce TB-COF as a pale yellow powder. Yield: 380 mg (86%). Anal. Calcd. for $(\text{C}_7\text{H}_4\text{BNO})_n$: C, 65.21; H, 3.13; N, 10.86. Found: C, 61.43; H, 4.46; N, 4.29. FT-IR (KBr, cm^{-1}): 3411 (w), 1612 (w), 1512 (s), 1412 (m), 1342 (s), 1182 (w), 1013 (m), 843 (w), 816 (m), 744 (m), 679 (w), 639 (w).

2.2. Synthesis of TB-COF/S composite

The as-prepared TB-COF (140 mg) was ground with sulfur (100 mg Sigma-Aldrich). The mixture was then sealed in a glass vial under

nitrogen atmosphere. The glass vial was heated at 160 °C for 12 h, and then further heated at 200 °C with a heating rate of 5 °C min^{-1} , the vial was kept at 200 °C for 3 h. After cooled to room temperature, TB-COF/S composite was obtained, the final mass fraction of sulfur in the composite was determined by TGA.

2.3. Visualized Li_2S_6 adsorption and ultraviolet absorption spectrum test

A Li_2S_6 stock solution of 10 mmol L^{-1} was firstly prepared through dissolving Li_2S (23 mg, 0.5 mmol) and element sulfur (80 mg, 2.5 mmol) in DOL/DME (1:1 by volume, 50 mL) under argon-filled glovebox. The TB-COF/S cathode piece was added into the solution, followed by mild magnetic stirring for 24 h to ensure thorough adsorption. The adsorption ability was visually detected by color change of the resultant solution, and blank Li_2S_6 solution was used as a reference. The resultant solution was further used for the ultraviolet absorption spectrum and blank Li_2S_6 solution was used as a reference.

3. Results and discussion

TB-COF was readily prepared by self-condensation reaction of 4-cyanophenylboronic acid in the presence of trifluoromethanesulfonic acid (TfOH) (Fig. 1a). The polymerizing process was monitored by Fourier transform infrared (FTIR) spectroscopy. The intensified peak at 1510 cm^{-1} and a new peak at 816 cm^{-1} are related to triazine absorption bands of TB-COF, verifying successful cyclotrimerization of cyano group (Fig. 1b) [33], while the appearance of a peak at 744 cm^{-1} indicates the formation of six-membered B_3O_3 boroxine ring [35]. Meanwhile, the characteristic peak of cyano group at 2230 cm^{-1} as well as hydroxyl group at 3410 and 3212 cm^{-1} disappear in 4-cyanophenylboronic acid, manifesting complete conversions of cyano and boronic groups. In solid-state ^{13}C NMR spectrum of TB-COF (Fig. S1), the formation of triazine linkage is further verified by the characteristic resonance peak of triazine carbon atoms at 170 ppm [33,42]. The signals in the range of 144–120 ppm are assigned to the carbon atoms of phenyl ring. The crystalline structure of TB-COF was resolved by using powder X-ray diffraction (XRD) measurement in conjunction with structure simulation. As shown in Fig. 1c, TB-COF exhibits an intense peak at 6.8° corresponding to (100) plane, along with minor peaks at 12.3, 14.3, 18.8 and 26.5° (black curve), which are assigned to (110), (210), (201) and (001) planes, respectively. The crystal model was generated using the Materials Studio software package. It can be visualized that the experimental XRD pattern matches well with simulated pattern (blue curve) of the eclipsed stacking model of TB-COF (Fig. 1d). Furthermore, the Pawley refinement gives an XRD pattern (red curve), which is in good agreement with the experimental pattern (green curve). According to the above results, a hexagonal unit cell based on $\text{P}\bar{6}$ m2 space group with parameters of $a = b = 15.02 \text{ \AA}$, $c = 3.48 \text{ \AA}$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ is deduced.

The morphology and microstructure of TB-COF were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM images show TB-COF is a densely packed structure consisting of tiny particles (Fig. S2a). TEM images corroborate the presence of evenly distributed micropores in TB-COF (Fig. 1e and Fig. S2b). The microporous nature of TB-COF was further validated by nitrogen sorption at 77 K. TB-COF gives a typical type I adsorption/desorption isotherm according to IUPAC classification (Fig. S3a). The sharp nitrogen uptake in low pressure region ($P/P_0 < 0.1$) is associated with extensive micropores. The Brunauer-Emmett-Teller (BET) specific surface area and pore volume are 708 $\text{m}^2 \text{ g}^{-1}$ and 0.28 $\text{cm}^3 \text{ g}^{-1}$, respectively. The pore size distribution shows pore size of TB-COF is predominantly 1.2 nm (Fig. S3b), which is consistent with the theoretical value predicted from its crystal structure. The high

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