



Tuning the Chemistry of Organonitrogen Compounds for Promoting All-Organic Anionic Rechargeable Batteries

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ABSTRACT

The ever-increasing demand for rechargeable batteries induces significant pressure on the worldwide metal supply, depleting resources and increasing costs and environmental concerns. In this context, developing the chemistry of anion-inserting electrode organic materials could promote the fabrication of molecular (metal-free) rechargeable batteries. However, few examples have been reported because little effort has been made to develop such anionic-ion batteries. Here we show the design of two anionic host electrode materials based on the N-substituted salts of azaaromatics (zwitterions). A combination of NMR, EDS, FTIR spectroscopies coupled with thermal analyses and single-crystal XRD allowed a thorough structural and chemical characterization of the compounds. Thanks to a reversible electrochemical activity located at an average potential of 2.2 V vs. Li⁺/Li, the coupling with dilithium 2,5-(dianilino)terephthalate (Li₂DAnT) as the positive electrode enabled the fabrication of the first all-organic anionic rechargeable batteries based on crystallized host electrode materials capable of delivering a specific capacity of ≈ 27 mAh/g_{electrodes} with a stable cycling over dozens of cycles (≈ 24 Wh/kg_{electrodes}).

KEYWORDS: organo-nitrogen, compounds, rechargeable, batteries, zwitterions, fabrication

I. INTRODUCTION

[Ru(NO)₂(PPh₃)₂] reacts with PhCH₂Br in hot toluene under CO to give [RuBr(CO)(NO)(PPh₃)₂], [RuBr₂(CO)₂(PPh₃)₂], PhCh=NOH, PhCN, and PhCONH₂, together with small amounts of PhCHO and PhCH₂OH; in the absence of CO, under N₂ or C₂H₄, the yields of organonitrogen products are reduced, and [RuBr₂(NCPH)₂(PPh₃)₂] and [RuBr₃(NO)(PPh₃)₂] are formed.[1,2,3]

Covalent organic frameworks with designable periodic skeletons and ordered nanopores have attracted increasing attention as promising cathode materials for rechargeable batteries. However, the reported cathodes are plagued by limited capacity and unsatisfying rate performance. Here we report a honeycomb-like nitrogen-rich covalent organic framework with multiple carbonyls. The sodium storage ability of pyrazines and carbonyls and the up-to twelve sodium-ion redox chemistry mechanism for each repetitive unit have been demonstrated by in/ex-situ Fourier transform infrared spectra and density functional theory calculations. The insoluble electrode exhibits a remarkably high specific capacity of 452.0 mAh g⁻¹, excellent cycling stability ($\sim 96\%$ capacity retention after 1000 cycles) and high rate performance (134.3 mAh g⁻¹ at 10.0 A g⁻¹). Furthermore, a pouch-type battery is assembled, displaying the gravimetric and volumetric energy density of 101.1 Wh kg⁻¹_{cell} and 78.5 Wh L⁻¹_{cell}, respectively, indicating potentially practical applications of conjugated polymers in rechargeable batteries.[5,7,8]

II. DISCUSSION

Covalent organic frameworks (COFs), which are a class of polymers with designable periodic skeletons and ordered nanopores, have been demonstrated potential applications widely in the fields such as catalysis, semiconductors, proton conduction, and gas capture¹⁻⁶. Moreover, COFs with controllable pore size and redox sites can also be applied in the field of electrochemical energy storage and conversion⁷⁻⁹. For efficient battery electrode applications,



the skeletons of COFs need contain active groups such as C=O and C=N bonds where O and N atoms could combine with ions (e.g. Li⁺, Na⁺, and K⁺)¹⁰⁻¹². In addition, the nanopores should be large enough to accommodate ions like Na⁺ without evident volume expansion and promote facile ions transport¹³. Generally, COFs-based electrode materials show the merits of low cost, environmental friendliness, structural designability, and sustainability^{14, 15}.

In fact, the application of COFs-based cathode materials for rechargeable batteries is just in the beginning^{16,17}. For example, Kaskel's group reported a microporous (1.4 nm) bipolar COFs with active triazine rings and inactive benzene rings in the skeletons as an organic electrode for sodium-ion batteries, showing specific capacities of ~200 and 10 mAh g⁻¹ at 0.01 and 10 A g⁻¹, respectively¹⁸. Subsequently, Wang's group designed three different types of exfoliated COFs for lithium batteries, exhibiting specific capacities of 145, 210, and 110 mAh g⁻¹ for anthraquinone-based, benzoquinone-based, and nitroxyl radical-based COFs, respectively¹⁹. Recent work revealed that the pentacenetetrone-based π -conjugated COFs with active C=O bonds and inactive linkage groups in the skeletons displayed a discharge capacity of ~120 mAh g⁻¹ at a high rate of 5.0 A g⁻¹ and a capacity retention of 86% after 1000 cycles at 1.0 A g⁻¹ in sodium batteries²⁰. The reported COFs-based cathodes for rechargeable batteries are still plagued by low capacity (~200 mAh g⁻¹) and inferior rate capability, limiting their further applications^{21,22}. The limited capacity of COFs-based cathodes can be ascribed to the introduction of inactive components (e.g., benzene skeleton, boronate esters, and hydrazones), which are used as the linkages to connect active groups within the molecules²³⁻²⁵. Additionally, the relatively poor electronic and ionic conductivities of the reported COFs-based electrode materials lead to their inferior rate capability^{26,27}. The reported method to improve the rate performance of COFs is combining with conductive carbon materials such as graphene²⁸⁻³⁰. However, the addition of too many carbon materials inevitably decreases the whole energy density of practical batteries. Overall, realizing COFs-based cathode materials with high capacity and high-rate performance is still challenging nowadays.[9,10,11]

Herein, we report the design, synthesis and battery application of a COF with triquinoxalinylene and benzoquinone units (TQBQ) in the skeletons via a triple condensation reaction between tetraminophenone (TABQ) and cyclohexanehexaone (CHHO). Benefiting from the absence of inactive linkage groups in the skeletons, the TQBQ-COF electrode shows a high reversible capacity of 452.0 mAh g⁻¹ and maintains 352.3 mAh g⁻¹ after 100 cycles at 0.02 A g⁻¹ in sodium batteries. Furthermore, the introduction of N atoms reduces the energy gap between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO), resulting in enhanced electronic conductivity (~10⁻⁹ S cm⁻¹) and high ionic conductivity (~10⁻⁴ S cm⁻¹ for the discharged product). As a result, the TQBQ-COF shows a high rate capability of 134.3 mAh g⁻¹ at 10.0 A g⁻¹. In addition, the insoluble TQBQ-COF electrode exhibits excellent cycling stability with a capacity retention of 96% after 1000 cycles at 1.0 A g⁻¹. Moreover, the combination of in/ex-situ Fourier transform infrared (FTIR) spectra and density functional theory (DFT) calculations demonstrate that the pyrazines (C=N) and carbonyls (C=O) are the active sites, and per TQBQ-COF repetitive unit could store twelve Na⁺ ions, including six Na⁺ ions within the TQBQ-COF plane and another six Na⁺ ions outside the plane. The Mulliken charges of the two types of Na atoms and their adjacent N and O atoms can be obtained according to the accurate atomic coordinates of Na₁₂TQBQ-COF. Furthermore, the average atomic valences of Na, O, and N in Na₁₂TQBQ-COF are calculated to be +1, -1, and -0.5, respectively. In addition, a pouch-type sodium battery with a capacity of 81 mAh is fabricated, showing the way for the application of large batteries.[18,17]

III. RESULTS

The electrochemical performance of the TQBQ-COF electrodes including galvanostatic charge/discharge, CV and EIS were evaluated in CR2032-type coin cells with sodium disks applied as the counter electrodes. Moreover, the glass microfiber membrane (Whatman GF/D, Aldrich) was used as the separator, and 1.0 M NaPF₆/DEGDME solution was applied as the electrolyte. The TQBQ-COF electrode was prepared by mixing 50 wt% TQBQ-COF powders, 40 wt% Super P and 10 wt% polyvinylidene fluoride (PVDF) in the homogenate locket, dispersing the mixture in anhydrous N-methyl-2-pyrrolidinone (NMP) and casting the resulting slurry on an Al foil, followed by



drying it at 80 °C in vacuum for 12 h. Finally, punched the Al foil into circular electrodes and stored them in Ar-filled glovebox before the assembly of the cells. Galvanostatic charge/discharge was performed on LAND-CT2001A battery instrument (LAND Electronic Co., Wuhan China). CV was carried out in the voltage range of 0.8~3.8 V at a scan rate of 0.2 mV s⁻¹ and EIS was carried out on a Parstat 263 A electrochemical workstation (AMETEK Co.) in a frequency range of 10⁵–0.01 Hz. With a cathode-limited design, the cell capacity was determined based on the mass of TQBQ-COF by deducting the capacity contribution from Super P.[12,13,15]

IV. CONCLUSIONS

To monitor the structural evolution of active materials in charge/discharge processes, the TQBQ-COF electrodes for in-situ FTIR measurement were containing 80 wt% active material, 10 wt% Super P, and 10 wt% PTFE. After hand mixing, the slurry was casted onto the stainless steel net, and the electrodes were dried at 60 °C for 12 h under vacuum. The process to prepare the cell for in-situ FTIR testing is in the Ar-filled glove box. During the test, a stream of Ar flow was used to protect the discharging/charging products from oxidized in attenuated total reflection (ATR) pattern. Based on the CV results, the assembled cells were cycled at a current density of 0.02 A g⁻¹ in the range of 0.8–3.7 V for in-situ FTIR measurements. TQBQ-COF electrodes for ex-situ FTIR testing contain 70 wt% active material, 20 wt% Super P, and 10 wt% PVDF. The preparation was made in the same way as the approach mentioned above. The samples for ex-situ FTIR tests were obtained by disassembling the labeled cells in the argon-filled glovebox, and washing the electrodes with glycol dimethyl ether (DME) for three times, followed by dried in vacuum. The products at different charge and discharge states were tested in a stream of Ar flow using the ATR pattern.[19,20]

TQBQ-COF electrodes for XPS testing contain 60 wt% active material, 30 wt% Super P, and 10 wt% PVDF. Samples were prepared by disassembling the labeled cells in the Ar-filled glovebox, and washing the electrodes with glycol dimethyl ether (DME) for three times, followed by dried in vacuum. Finally, the products at different charge and discharge states were tested in the argon atmosphere.

Becky's three-parameter exchange function combined with Lee-Yang-Parr correlation functional (B3LYP) method with 6–31 G (d) basis set⁴⁰ was applied for the geometric optimization of the TQBQ-COF. All molecular structures were optimized using Gaussian 16 software package under B3LYP/6–31 G (d) level of theory followed by vibrational frequency calculations and to further confirm their stability. To simulate the solvation effect, single point energy calculations were performed using the SMD solvation model at B3LYP/6-31 + G (d, p) level with a solvent dielectric constant (ϵ)⁴¹ of 7.2 which reliably describes the polarity of experimentally used electrolyte solvent DEGDME. The molecular electrostatic potential (MESP) method was applied to predict the sodiation sites of TQBQ-COF using Multiwfn 3.6 software⁴², by which the Mayer bond order analysis⁴³ and the density of states (DOS) were also carried out. In addition, the accurate atomic coordinates of Na₁₂TQBQ-COF were calculated by Gaussian 16 software package, from which the Mulliken charges of two types of Na atoms and their adjacent N and O atoms can be obtained.

The sodiation/desodiation process of the potential active sites was revealed by orbital composition analyses of the lowest unoccupied molecular orbital (LUMO), to clarify the stabilization effect of both nitrogen and oxygen atoms towards sodium ions. The MESP of TQBQ-COF and Na₆TQBQ-COF were calculated to find the rest of Na⁺ accommodation sites.[21]

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