Inorganic Chemistry

Mesoporous MnO/C–N Nanostructures Derived from a Metal– Organic Framework as High-Performance Anode for Lithium-Ion Battery

Ji-Liang Niu,[†] Gui-Xia Hao,[‡] Jia Lin,[†] Xiao-Bin He,[†] Palanivel Sathishkumar,[§] Xiao-Ming Lin,^{*,†,§}

[†]Guangzhou Key Laboratory of Materials for Energy Conversion and Storage, School of Chemistry and Environment, South China Normal University, Guangzhou 510006, P. R. China

[‡]College of Chemistry and Environmental Engineering, Hanshan Normal University, Chaozhou, Guangdong 521041, P. R. China [§]Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, School of Chemistry and Environment, South China Normal University, Guangzhou 510006, P. R. China

S Supporting Information

ABSTRACT: By application of newly designed ligand 5-(3-(pyridin-3-yl)benzamido)isophthalic acid (H₂PBI) to react with Mn(NO₃)₂ under solvothermal conditions, a 2-fold interpenetrated Mn-based metal–organic framework (Mn-PBI) with rutile-type topology has been obtained. When treated as a precursor by pyrolysis of Mn-PBI at 500 °C, mesoporous MnO/C–N nanostructures were prepared and treated as an lithium-ion battery anode. The MnO/C–N manifests good capacity of approximately 1085 mAh g⁻¹ after 100 cycles together with superior cyclic stability and remarkable rate capacity, which is supposed to benefit from a large accessible specific area and unique nanostructures. The remarkable performances suggest promising application as an advanced anode material.



1. INTRODUCTION

Nowadays, lithium-ion batteries (LIBs) have been highly attractive for large-scale applications of electrical and hybrid electrical vehicles on account of their efficacy in high energy density, long cycle life, high specific capacity, high operating voltage, and no memory effect.¹ Previously, graphite,² metal,³ metal $oxide_1^4$ and organic electrode materials⁵ have been intensively investigated and used for batteries. However, their large-scale applications and further development have been impeded due to certain limitations, including cell failure and poor capacity retention.⁶ Moreover, small organic molecules have the drawbacks of low thermal stability and solubility in organic electrolytes in comparison to those of inorganic molecules.⁷ These limitations are still long-term challenging issues in the development of appropriate electrode materials for LIBs. Generally speaking, three strategies could be undertaken to solve these obstacles. First, nanostructured materials can offer a continuous electron pathway and greatly shorten the length of charge diffusion, which is crucial to rate capability. For example, nanotubes,⁸ nanowires,⁹ nanoplates,¹⁰ nanospheres,¹¹ and core/shell structures¹² show remarkable electrochemical performance due to their unique nanoarchitectures. Second, porous characteristics and large surface area can provide more reaction sites and enlarge contact areas between the electrolyte and active materials. Third, incorporation of the optimized N-

dopant concentration into the networks can introduce more defects to improve the electrochemical properties in the application of LIBs.¹³

Metal-organic frameworks (MOFs), as a functional family of inorganic/organic hybrid materials with high porosity and large surface area, have shown great promise for their applications as new electrode materials for LIBs.¹⁴ The increasing amount of research demonstrates that MOFs could be successfully employed as effective sacrificial templates or precursors to fabricate metal oxides with an excellent lithium storage property through a high-temperature calcination process.¹⁵ In particular, metal oxides derived from MOFs can be size- and shapecontrolled by adjusting the preparation conditions. For example, porous MoO_2 nano-octahedrons,¹⁶ spherical-shaped CuO nanoparticles,¹⁷ urchin-like Mn₃O₄ microspheres,¹⁸ hollow Co₃O₄ parallelepipeds,¹⁹ hierarchical porous anatase $\text{TiO}_{2^{\prime}}^{20}$ spindle-like mesoporous α -Fe₂O₃²¹ and so forth were fabricated using suitable MOFs as templates and displayed excellent electrochemical performances. Inspired by these great achievements received to date, the present work mainly focuses on controlling the morphology of the MOF-derived metal oxide and further development as advanced anode materials. In

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this work, a novel ligand, 5-(3-(pyridin-3-yl)benzamido)isophthalic acid (H_2PBI , Scheme S1) was designed and synthesized using isophthalate and pyridine as terminal groups, connected through amide bonds, to construct a porous Mnbased MOF with 2-fold interpenetrated rutile topology. Direct pyrolysis of this MOF gave rise to mesoporous MnO/C–N nanostructures, which could be used as an LIB anode with improved reversible capacity and excellent cyclability.

2. EXPERIMENTAL SECTION

2.1. Materials Characterization. Functional groups of the materials were assessed using Fourier transform infrared spectroscopy (Thermo Nicolet NEXUS 670 FT-IR, USA). Elemental analyses were carried out using an elemental analyzer (PerkinElmer 240, USA). Crystalline phase was identified by a Bruker D8 Advance X-ray diffraction pattern diffractometer (BRUKER-AXS, Germany). Raman spectra were obtained from a Renishaw inVia confocal Raman microscope (UK). Netzsch Thermo Microbalance TG 209 F1 Libra (Germany) was used for thermogravimetric analyses (TGA) to determine the thermal behavior (mass) of the material. The sorption isotherms were assessed using a Belsorp max gas sorption analyzer (Japan) at 77 K. X-ray photoelectron spectroscopy (XPS) was recorded by ESCALAB 250Xi XPS spectrometer (USA). The surface morphology and architecture were recorded by scanning electron microscopy (SEM, TESCAN Maia 3, Czech) and transmission electron microscopy (TEM, JEM-2100HR, Japan). A Varian Mercury Plus 300 MHz spectrometer was used to record ¹H NMR spectra (USA).

2.2. Preparation of the Mn-PBI MOF. The synthetic route of the H₂PBI ligand is given in Scheme S1, and the obtained ligand was further confirmed by its H¹ NMR spectrum (Figure S1). To a mixed solvent of dimethylformamide (DMF, 3 mL) and ethanol (3 mL) in a 20 mL scintillation vial were added H₂PBI (18 mg, 0.05 mmol) and $Mn(NO_3)_2$ ·4H₂O (25 mg, 0.1 mmol). The capped vial was heated at 80 °C at a rate of 0.5 °C/min for 32 h. After cooling, pale pink crystals of Mn-PBI were obtained (yield: 75.3%) by filtration. IR: 3519, 3453, 1650, 1564, 1423, 1373, 1318, 774, 723 cm⁻¹ (see Figure S3). Elemental analysis (% calcd/found): C, 56.57/56.59; N, 8.60/8.57; H, 3.92/3.91.

2.3. Electrochemical Measurements. The MnO/C–N electrode was prepared by annealing of Mn-PBI MOF as templates at 500 °C for 3 h under a N₂ atmosphere. Electrochemical behavior of MnO/C–N electrode was assessed by coin-type half cells (2025 type) separated by a celgard 2400 membrane. LiPF₆ (1 M) was dissolved in diethyl carbonate and ethylene carbonate in a volume ratio of 1:1 as electrolyte. The mixture of active material, polyvinylidene fluoride (PVDF), and super P carbon black binder in the ratio of 7:1:2 (w/w) was coated onto a piece of copper foil and then was placed in an oven at 70 °C for 1 day. LAND CT2001A multichannel battery testing system was applied to detect the galvanostatic charge/discharge between 0.01 and 3.0 V. The cyclic voltammetry (CV) measurements were scanned at 0.05 mV s⁻¹ from 0.01 to 3.0 V with an Electrochemical Workstation (CHI660C).

2.4. X-ray Crystallographic Studies. X-ray reflection intensities were performed with a Bruker APEX II diffractometer at 296 K using graphite monochromatic Mo K α radiation ($\lambda = 0.71073$ Å). The empirical absorption corrections were used to correct the reflections, and the structure was refined by full-matrix least-squares on F^2 using the SHELXL programs (SHELXTL-2014).²² The isotropic displacement parameter was used to place the organic hydrogen atoms in calculated positions. The details of the crystal parameters and refinement are presented in Table S1. Table S2 presents the selected bond lengths and angles. CCDC 1534095 contains the crystallographic data.

3. RESULTS AND DISCUSSION

3.1. Structure and Characterization of Mn-PBI MOF. Mn-PBI were successfully prepared by reacting H₂PBI with manganese nitrate in a mixture of DMF- C_2H_5OH at 80 °C for 72 h. Mn-PBI possesses a 2-fold interpenetrated (3,6)-connected three-dimensional (3D) structure. As depicted in Figure 1a, each Mn(II) coordinates with four oxygen atoms



Figure 1. Mn-PBI: (a) Coordination environment of Mn(II), (b) 3D structure with space filling, (c) 2-fold interpenetrated structure, and (d) schematic representation of the self-interpenetrated (3,6)-connected rutile topology. All hydrogen atoms are omitted for clarity.

(O1, O3A, O4A, and O2B), one nitrogen (N1C) from four different PBI ligands, and one coordinated DMF molecule to furnish a distorted octahedral geometry. The Mn–O bond lengths are in the range of 2.092(3)-2.315(5) Å, which are comparable to the expected values for Mn(II)–O in the previous reports.^{23,24}

Two adjacent Mn ions are connected between the isophthalate groups, generating a 1D linear chain with binuclear [Mn₂(COO)₄] units (Figure S4). Moreover, each PBI ligand employs its one pyridyl and two carboxylate groups in turn to link another four metal atoms, generating a 3D framework with 1D rectangular channel (Figure 1b). It is worth mentioning that one 3D net combines with another identical one, leading to the formation of a self-interpenetrated structure (Figure 1c). A similar 2-fold interpenetrated network can be observed in previous literature.^{25,26} After omitting the DMF molecules, PLATON²⁷ analysis indicates that solvent accessible volume is 23.3% per unit cell volume [489.6/2097.3 Å³]. If each PBI²⁻ ligand serves as a three-connector and each Mn(II) acts as a three-connecting node, then Mn-PBI represents a 2-fold interpenetrated (3,6)-connected rutile net with the Schläfli symbol of $(4^2 \cdot 6^{10} \cdot 8^3)$ $(4 \cdot 6^2)_2$ simplified by TOPOS (Figure $(1d)^{28}$

The morphology of Mn-PBI particles was observed by SEM analysis. The surfaces of the Mn-PBI MOFs are smooth and have cubic-like shape with the sizes of tens of microns (Figure S6). The powder X-ray diffraction (PXRD) pattern shows that most diffraction peaks are well matched with the simulated pattern results, confirming the phase purity of the bulk sample (Figure S7). The TG curve shows that an initial loss (15.3%) was observed within 150–300 °C due to the release of a DMF molecule (calcd 15.0%). The further weight loss between 300 and 500 °C is ascribed to decomposition of the framework (Figure S8). N₂ adsorption/desorption isotherms present



Figure 2. MnO/C–N electrode: (a) XRD, (b) Raman spectrum, (c) XPS spectrum, and (d) N_2 adsorption–desorption isotherms with inset poresize distribution.

typical type-I microporous characteristics with a surface area of 525 m² g⁻¹ (Figure S9). According to the TGA result, Mn-BPI samples in our case were calcined at 500 °C by one-step thermal treatment under a flow of air to ensure complete conversion of precursors to the final products.

3.2. Characterization of the MnO/C-N Materials. XRD analysis in Figure 2a confirmed that the obtained product after pyrolysis was composed of monoclinic cubic structure space group Fm3m of MnO phase (JCPDS No.07-0230). Raman spectrum reveals two weak bands at 550 and 644 cm⁻¹ are indexed to the typical characteristic of the MnO (Figure 2b).^{29,30} Obviously, two other broad peaks at 1357 cm⁻¹ for Dbond (disordered carbon) and 1597 cm⁻¹ for G-bond (ordered graphitic carbon) are also detected simultaneously.³¹ In addition, the intensity of the G peak is greatly enhanced compared to that of the D peak with a high $I_{\rm G}/I_{\rm D}$ band intensity ratio of \sim 1.20, which suggests the greatly increased graphitization degree of the carbon for the final samples.³² For the chemical state and composition to be examined further, Xray photoelectron spectroscopy (XPS) spectra were recorded. The characteristic peaks of C 1s, N 1s, O 1s, and Mn (2s, 2p, 3s, and 3p) were observed in a wide scan spectrum in Figure 2c, further confirming the successful synthesis of MnO/C-N. Two major peaks at 641.3 and 652.9 eV are detected in the highresolution XPS of Mn(II) 2p (Figure S10), corresponding to Mn $2p_{3/2}$ and Mn $2p_{1/2}$, respectively. These results are well matched with MnO.³³ The C 1s XPS peaks can be fitted into four parts at 284.6 eV (C-C), 285.6 eV (C-O), 286.3 eV (C=O), and 288.4 eV (O=C-O), respectively.³⁴ The N 1s spectrum shows three components at 399.1 eV (pyridinic (N-6)), 400.9 eV (pyrrolic (N-5)), and 401.5 eV (graphitic (N-Q)

type N atoms).³⁵ Peaks at 530.1 and 531.6 eV correspond to the O in Mn–O and C–O, respectively.³⁶ On the basis of XPS analysis, the elemental contents of C and N were 12.18 and 5.10 wt %, respectively. N2 adsorption-desorption isotherms were measured to evaluate the porosity of Mn/C-N composites. Figure 2d exhibits clear type IV with hysteresis loops, indicating the mesoporous characteristics (IUPAC classification). The Barrett-Joyner-Halenda (BJH) method was applied to calculate the pore-size distribution. The result shows the existence of two kinds of mesopores with sizes of 13 and 26 nm. The Brunauer-Emmett-Teller (BET) result confirms the surface area is 146.4 $m^2 g^{-1}$ and the pore volume is $0.59 \text{ cm}^3 \text{ g}^{-1}$. This mesoporous structure and large surface not only provides a convenient pathway to electrolyte diffusion and Li-ion transfer but also facilitates accommodating the volumetric variations during the lithium storage process, which is highly favorable for the electrochemical performance enhancement as electrode.

For better observation of the morphology and architecture of the Mn/C–N composite, SEM and TEM were applied. Compared to the Mn-MOF precursor, the shape of MnO/ C–N was retained well, whereas the size slightly shrinks ranging from 5 to 10 μ m due to decomposition and volume contraction after calcination (Figure 3a). The surface becomes relatively rough, and many tiny nanoparticles can be clearly observed on the surface (Figure 3b). The surface of the material was decorated with many holes due to the formation of pores during the thermal treatment (Figure 3c). The TEM image in Figure 3d further confirms its nanoparticles with size of less than 20 nm. The interplanar lattice fringe distance is found to be 0.26 nm depicted in the high-resolution TEM



Figure 3. MnO/C-N composite: (a, b) low- and (c) highmagnification SEM images, (d) TEM and (e) HRTEM images with selected-area electron diffraction pattern, and (f) EDS mapping images.

(HRTEM) image (Figure 3e), which is indexed to the (111) lattice plane of cubic MnO. Selected-area electron diffraction (SAED) pattern (inset in Figure 3e) clearly shows a well-defined crystalline structure. Additionally, energy-dispersive spectroscopy (EDS) element mapping images further reveal the presence of O, N, C, and Mn elements (Figure 3f) in agreement with the XPS analysis.

3.3. Electrochemical Analysis. The MnO/C-N electrode exhibited excellent lithium storage performance when evaluated as an anode for LIBs. CV curves were scanned at a rate of 0.05 mV s^{-1} . As depicted in Figure 4a, three reduction peaks were observed in the first cathodic sweep. The sharp peak appearing at 0.16 V results from the reduction of Mn^{2+} to $Mn^{0.37,38}$ The reaction can be described as follows: MnO + $2Li^+ + 2e^- \rightarrow Mn$ + Li₂O. However, this peak shifted to approximately 0.2 V in the second cycle, which is ascribed to the Li₂O and metallic manganese formation, indicating an irreversible phase transformation.³⁹ A small reduction peak was detected at 0.61 V and then disappeared after subsequent cycles, which indicates the generation of a solid electrolyte interface (SEI) layer with irreversible reduction of electrolyte.^{40,41} A reduction peak near 0.84 V corresponds to the reduction of Mn^{3+}/Mn^{4+} to Mn^{2+} . The oxidation peak appearing at 1.01 V in the anodic scan performance is due to the oxidation reaction of Mn^0 to Mn^{2+} (Mn + Li₂O \rightarrow MnO + 2Li⁺ + 2e⁻),^{42,43} which remained after further cycling. In the meantime, one weak peak located at 1.77 V was also detected, which can originate from the reoxidation of Mn(II) to a higher oxidation state.⁴⁴⁻⁴⁶ The XPS spectrum

was recorded to examine valence states of manganese after the first charge process. As shown in Figure S11, after a peak fitting deconvolution, the species of Mn^{4+} (644.1 eV), Mn^{3+} (642.9 eV), and Mn^{2+} (641.2 eV) could be observed, which indicates the presence of Mn^{4+} and Mn^{3+} valence states in the electrode after the first charge, further accounting for the appearance of a peak at 1.77 V in the CV curves. The subsequent CV curves become stable and overlap, indicative of good reversibility.

Figure 4b demonstrates the galvanostatic charge/discharge within 0.01-3.0 V at 300 mA g⁻¹. In the first discharge process, it clearly shows that a distinct long voltage plateau was found around 0.2 V, which can be assigned to the reduction of Mn²⁺ to Mn⁰. The discharge plateau increases to 0.5 V in the second cycle, arising from the formation of Li₂O and Mn (irreversible structural transformation). The MnO/C-N composite electrode delivers approximately 1507 mAh g^{-1} as the first discharge capacity and 1143 mAh g^{-1} as the charge capacity. The initial loss of capacity with a Coulombic efficiency of 75.8% might be due to the inevitable decomposition of the electrolyte and SEI layer, which is regarded as an irreversible electrochemical reaction. Despite the initial capacity loss, the chargedischarge profiles are basically invariable without capacity fading from the subsequent cycles. Interestingly, a discharge capacity of 1085 mAh g⁻¹ was retained after the 100th cycling (Figure 4c). Meanwhile, Coulombic efficiency maintained almost 100% after initial cycles, which confirms the reusability of the MnO/C-N composite electrode. Figure 4d illustrates the rate capacities of the MnO/C-N electrode. When the current densities rise from 0.3 to 0.5, 1, 2, and 3 A g^{-1} , the capacity decreased from 1085 to 924, 877, 775, and 665 mAh g⁻¹, respectively. Surprisingly, even at a high current density of 5 A g^{-1} , a high capacity of 552 mA h g^{-1} was still retained. In addition, when the current density was restored to 0.3 A g^{-1} , the fabricated electrode almost recovered its original capacity, which proved the excellent rate capability. This observed excellent capacity is considerably higher than that of MnO with a theoretical value of 765 mAh g^{-1} and other MnO hybrid anode materials reported previously (Table S3). Moreover, in comparison with other MOF-derived porous MnO materials, our Mn/C-N electrode shows competitive reversible capacity and more superior rate capacity. In particular, it delivers a capacity of up to 665 mAh g^{-1} even at 5 A g^{-1} , proving longterm cycling stability and also incomparable high-rate performance.

Calcination temperature is also one of the important parameters to obtain preferred electrode materials while using MOFs as sacrificial templates. For comparison, Mn-PBI MOFs were calcined at different temperatures. The similar PXRD patterns confirm the cubic MnO phase after the thermal transformation process (Figure S12). Apparently, the obtained Mn/C-N electrode material calcined at 500 °C exhibits the highest discharge capacity compared with the materials pyrolyzed at 600 and 700 °C (Figure 5a). From the SEM images in Figure S13, some of the final products were found to collapse at 600 °C. Moreover, the initial morphology totally disappeared, and some agglomerates with nonregular shape were obtained at a higher temperature (700 °C). Thus, it is highly essential to control the heating temperature for the conversion of the Mn-PBI MOF template into the desired architecture. As demonstrated in previous literature, the amount of N-doping composition could improve lithium storage capacity.^{47,48⁻} The N content of MnO/C-N-500 (5.10 wt %) is larger than that of MnO/C–N-600 (4.29 wt



Figure 4. MnO/C–N electrode: (a) CV curves, (b) voltage profile at 300 mA g^{-1} ranging from 0.01 and 3.0 V, (c) cycle performance and Coulombic efficiency curves, and (d) rate performance at different current densities.



Figure 5. Mn-PBI MOFs pyrolyzed at different temperatures: (a) cycle-life performances at 0.3 A g^{-1} and (b) Nyquist plots for the three electrode materials.

%) and MnO/C–N-700 (4.04 wt %). Specifically, the total pyrrolic (N-5) and pyridinic (N-6) N atoms are as much as 75 at % in the MnO/C–N-500 samples (Figure S14 and Table S4), making the structure electron deficient, which can more strongly bind lithium atoms and accept more charge from Li ions.^{49,50} Electrochemical impedance spectra were also carried out (Figure 5b). In the region of high-to-medium frequencies, there is a depressed semicircle for all of the curves associated with charge-transfer resistance (R_{ct}) between electrolyte and electrode. A sloping line in the low frequency region can be found, which is related to diffusion of lithium inside the electrode (Warburg diffusion resistance, R_w). Evidently, the porous MnO/C–N after thermal treatment at 500 °C shows smaller R_{ct} compared to those of the other two materials obtained at 600 and 700 °C, suggesting better charge transfer

kinetics.⁵¹ These results also proved the superior electrochemical performance of MnO/C–N obtained at 500 $^{\circ}$ C.

4. CONCLUSIONS

In summary, a 2-fold interpenetrated MOF with (3,6)connected rutile topology was obtained by application of a new ligand to assemble with Mn(II) ions. Mesoporous Mn/C– N was successfully prepared through calciantion of the title MOF as a precursor. The resultant Mn/C–N nanoparticles delivered a high capacity of 1085 mAh g⁻¹ together with superior cyclic stability and good rate capacity. The improved lithium storage is supposed to benefit from the large accessible specific area and unique nanostructures. The remarkable performance makes it a promising LIB anode.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01486.

Experimental details, XRD patterns, TGA curve, XPS spectrum, and SEM images, and crystallographic data (PDF)

Accession Codes

CCDC 1534095 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: linxm@scnu.edu.cn. *E-mail: caiyp@scnu.edu.cn.

ORCID 0

Xiao-Ming Lin: 0000-0001-8835-103X

Notes

The authors declare no competing financial interest.

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