Inorganic Chemistry Cite This: Inorg. Chem. XXXX, XXX, XXX-XXX

Exploring the Capacity Limit: A Layered Hexacarboxylate-Based Metal–Organic Framework for Advanced Lithium Storage

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Supporting Information

ABSTRACT: Our previous work suggested that more carboxylate groups might lead to higher energy density for metal-organic frameworks. In this study, we synthesized a layered metal-organic framework (MOF) Ni-BHC by use of 1,2,3,4,5,6-benzenehexacarboxylic acid. After evacuation by thermal treatment, this MOF was employed as an anode for lithium storage. For its rich lithiation sites as well as layered fast-kinetics structure, it delivers a superior reversible capacity of 1261.3 mA h g⁻¹ at 100 mA g^{-1} , far exceeding the performance of previously reported MOF-based anode materials. Density functional theory calculation and O soft X-ray absorption spectroscopy suggest that the luxuriant carboxylate-metal units play an important part in the electrochemical process.



■ INTRODUCTION

Nowadays, the application of rechargeable lithium-ion batteries (LIBs) is extended to various fields, including small hand-held electronic devices, electric vehicles, and electrical energy storage. However, the commercial anodes, including graphite and lithium titanate, possess only limited theoretical capacities; hence, exploitation of high-capacity anode materials is of crucial importance for future needs.

Metal-organic frameworks (MOFs) or coordination polymers (CPs), being a kind of organic inorganic hybrid, have become an academic hot point for their changeable components, which can further help to adjust their structures, chemical activities, and pore sizes in wide ranges for the critical applications of sensing, proton conductivity, gas storage, and catalysis.²⁻⁶ Recently, the electrochemical applications of MOFs, especially in LIB anode materials, have developed rapidly and exhibited tremendous potential due to their abundant electroactive sites and large ion diffusion channels,⁷⁻¹¹ as summarized in Table S1. In these MOFs, carboxylate groups (e.g., 1,4-benzenedicarboxylate and 1,3,5-benzenetricarboxylate) are widely employed. It was found that in the electrochemical process, lithium is reversibly inserted to the organic components, especially the carboxylate groups;¹²⁻¹⁴ meanwhile, the coordinated metal ions might also be involved in the lithiation processes of these MOFs.¹⁵⁻¹⁷ Other functional groups such as imidazole,¹⁸ pyridine,¹⁹ and purine²⁰ always lead to low reversible capacity.^{14,21,22} Consequently, increasing the content of carboxylate groups might be a feasible method to further improve the capacities of MOFs.

To cater to this strategy, we choose an intriguing linkermellitic acid to construct such high-capacity MOFs for its abundant carboxylate groups. Mellitic acid, which is also known as 1,2,3,4,5,6-benzenehexacarboxylic acid, has six carboxylate groups, which have rich lithiation sites to boost the capacity.

As a proof-of-concept, a layered metal-organic framework named Ni-BHC was successfully synthesized here. This MOF is composed of 1D coordination chains based on two kinds of 6-coordinated nickel(II) clusters, and the chains are further piled up into 2D layers via hydrogen bonding and finally assembled into a 3D layered framework structure. After removing the coordinated water,^{23,24} we investigated the Li-storage performance of this material in the potential range of 0.01-3.0 V versus Li/Li⁺. This MOF exhibits a high capacity of 1664.4 mA h g^{-1} after 5 cycles and 1261.3 mA h g⁻¹ within 50 cycles, outperforming all the other MOF anodes reported to date as far as we know. Our work demonstrates the success of designing highperformance MOF anode for Li-ion batteries by increasing the content of carboxylate-metal units within a proper topology choice.

EXPERIMENTAL SECTION

Synthesis. The solvents and reagents were purchased from Innochem and used without further purification. In an optimized synthesis procedure, 0.5 mmol mellitic acid and 1.5 mmol Ni(NO₃)₂·6H₂O were dissolved in 10 mL of deionized water to produce a settled solution. Then, its pH was in situ measured by a pH meter, and 0.1 M NaOH was slowly added into the solution with stirring until pH \approx 3.2. The mixture was filtered and placed into an autoclave with Teflon-lined stainless at 130 °C for 1 day. Upon cooling to room temperature, the precipitates were filtered, and green single crystals (Ni-BHC) were obtained. The crystal sample was washed with water and allowed to air-dry (yield 43%). Evacuated Ni-BHC was prepared by annealing Ni-BHC at 220 °C in air for 3 h. Elemental analysis calcd for C12H36Ni3O30 (*M*_r = 836.48): C, 17.21; H, 4.3; Ni, 21.05; O, 57.38. Found: C, 16.82; H, 3.83; Ni, 22.29; O, 57.39. Main IR (KBr, cm⁻¹): 3590 m, 3315 m br,

Received: December 7, 2017

Article



Figure 1. (a) Coordination mode of the mellitic acid ligand in Ni-BHC. (b) Complex hydrogen-bonding interactions inside and between the layers of Ni-BHC observed along the *c*-axis.

1666 w, 1575 s, 1444 s, 1341 s, 1187 w, 991 w, 914 m, 719 m, 599 m, 555 m, 493 m, 421 w.

Physical Characterization. Inductively coupled plasma optical emission spectrometry (ICP/OES) analysis of Ni was conducted using a Varian 720-ES ICP/OES spectrometer. Elementar Vario ELIII analyzer was used to analyze elemental composition. Fourier transform infrared spectroscopy (FTIR) analyses were performed at a Nexus670 infrared spectrometer (Nicolet). X-ray Diffraction (XRD) data were recorded at an X-ray diffractometer (Rigaku Ultima IV) with Cu K α radiation. Thermogravimetric (TG) curves (heating rate: 10 °C min⁻¹) were obtained on a thermo-analyzer (STA 449 F3 Jupiter) under air atmosphere. An S-2400 scanning electron microscope (Hitachi, Japan) was employed to take SEM images. The soft X-ray absorption spectroscopy (sXAS) data were measured at Shanghai Synchrotron Radiation Facility (BL08UA). To conduct an ex situ sXAS test, the cell was first discharged or further charged to the desired voltages at 100 mA g^{-1} on the basis of cyclic voltammetry curves (Figure S6). Then, the cells were disassembled, and the electrodes were washed with the solvent of dimethyl carbonate (DMC) for a few times in an argon filled water-free and oxygen-free glovebox before ex situ tests.

Electrochemical Testing. The active material, conducting Super-P carbon black, and poly(acrylic acid) binder with weight ratios of 7:2:1 were stirred in solvent *N*-methyl-2-pyrrolidone for several hours to obtain a homogeneous slurry. Then, a Cu foil was used to load the obtained slurry before vacuum drying at 110 °C for half a day. We punched the electrodes into round wafers (diameter: 14.0 mm; loading: ~1.2 mg/cm²). The electrolyte is a mixed solvent of dimethyl carbonate (DMC), ethylene carbonate (EC), and ethyl methyl carbonate (EMC) (1:1:1, volume ratio) with 1 M LiPF₆. Finally, we assembled coin cells (CR2032) using the electrode, a lithium wafer, a Celgard 2325 separator, and the as-prepared electrolyte in the waterfree and oxygen-free glovebox filled with argon. A LAND 2001A battery tester and an electrochemical workstation (CHI660e) were employed to perform the electrochemical testing.

RESULTS AND DISCUSSION

Structures of the MOFs. In a previous report,²⁵ a roomtemperature synthetic method was employed, which requires a long reaction time of several weeks, thus limiting its practical application. In this work, a facile solvothermal method was proposed with reduced reaction time of just 1 day. The solvothermal reaction of Ni(NO₃)₂·6H₂O and mellitic acid in deionized water would generate green columnar crystals of Ni-BHC. During the synthesis process, NaOH dilute solution was used as a base to deprotonate the mellitic acid. A proper pH of 3.2 can greatly improve the quality of the Ni-BHC crystal. The morphology of the obtained Ni-BHC crystal is displayed in Figure S1.

As isomorphic compound of previous reported Co-BHC,²⁶ orthorhombic Ni-BHC crystallizes in the space group Pbca, and the whole molecule (containing two asymmetric units) contains three nickel ions, a mellitate ligand, and 18 molecules of water, giving a molecular formula of $[Ni_2(H_2O)_{10}][Ni(H_2O)_2(C_{12}O_{12})]$. $6H_2O$ (CCDC: 1009819).²⁵ Two kinds of Ni(II) node with octahedral geometries are connected by six oxygen atoms from mellitate ligands and water molecules to form the secondary building block, in which the Ni-O distances are in the range of 2.0431(15)-2.0987(15) Å. The coordination environments of Ni1 and Ni2 are very different. As shown in Figures 1a and 2a, Ni1 is surrounded by four carboxylate oxygen atoms and two water molecules, serving as the basic metal node to form 1D chain, while two Ni2 atoms ligated by one carboxylate oxygen atom and five water molecules are located on both sides of the 1D chain. In this molecule, 12 water molecules (O1W \sim O6W) are connected with the nickel ions to form octahedral NiO₆, and the residual 6 water molecules (O7W \sim O9W) are unconnected. Due to the abundant water molecules in the MOF, hydrogen-bonding interactions are found throughout the structure, as shown in Figure 1b. Oxygens from carboxylate moiety act as hydrogen atom acceptors, and coordinated water molecules from octahedral NiO₆ act as hydrogen atom donors, forming intrachain (1D) or intralayer (2D) hydrogen bonding to build a 2D layer. Water molecules coordinated with Ni1 and Ni2 can also form intralayer hydrogen bonding with each other (O1W-O4W and O2W-O6W). Thus, as shown in Figure 2b, the 1D chain, parallel to the *b*-axis, is piled up to one another via such hydrogen bonding to form a 2D layer. Eventually, as shown in Figure 2c, the as-formed 2D layers with a large lamellar spacing of 8.5285 Å are further connected along the *a*-axis via the hydrogen-bonding interactions formed through unconnected water molecules (O7W \sim O9W).

Physical Property. In previous work, we demonstrated the disadvantages of coordinated solvent in MOFs for Li storage.^{23,24} The major reasons are (1) solvent, especially water, might irreversibly react with the active lithium to form Li_2O or serve as



Figure 2. Hierarchical structure of Ni-BHC. (a) 1D chain parallel to the *b*-axis (blue: Ni1 octahedral geometries, yellow: Ni2 octahedral geometries). (b) 2D layer parallel to the *b*-axis. (c) The whole 3D chain-layer structure with the unit cell edges. Hydrogen atoms are omitted for clarity.

channel fillers, which will remarkably impede the Li-ion diffusion. (2) Solvent, especially water, might also react with LiPF₆ in electrolyte to form detrimental HF, which will destroy the electrode. (3) A high content of coordination solvent molecules can lower the content of reversible lithiation sites, thus lowering the specific capacity. For such reasons, MOFs especially with high content of solvent should be evacuated before being applied to Li storage.

Thermal treatment in proper temperature according to the TGA curve should be the most feasible method to remove solvent from materials. As displayed in Figure 3a, the first weight loss of ~40% between 100 and 300 °C in TGA curve of Ni-BHC can be attributed to the liberating of coordinated water (calcd 38.73%), and the following weight loss of \sim 40% at 350 °C can be ascribed to the pyrolysis of the organic linkers. There is no further weight loss with further rising of the temperature, leading to 24.65% NiO proved in Figure S2. To remove the coordinated water molecules while retaining the MOF skeleton, a proper temperature of 220 °C was selected to dry the Ni-BHC in air for 3 h, during which the green hydrous Ni-BHC converted to yellow anhydrous evacuated Ni-BHC, as displayed in Scheme S1. The TGA curve of the evacuated Ni-BHC was also plotted in Figure 3b, and there is only weight loss at 300-400 °C, demonstrating that the water molecules in the framework were almost thoroughly removed after the thermal treatment. For the evacuated Ni-BHC, 41.13% NiO is retained after complete calcination, corresponding to a formula of $Ni_3C_{12}O_{12}$.

Figure 3b shows the Fourier transform infrared spectra of mellitic acid, the fresh and evacuated Ni-BHC. The characteristic bands of mellitic acid at 1250, 1717, and 3010 cm⁻¹ ascribed to ν (C–O), ν (C==O), and ν (OH) of its nonionized –COOH disappear, while the new bands of Ni-BHC appeared at 1444 and 1575 cm⁻¹ can be assigned to the symmetric stretching vibrations and asymmetric stretching vibrations of –COO⁻, indicating the deprotonation of – COOH after coordinating with Ni(II). For Ni-BHC, there is a strong and broad peak centered at 3300 cm⁻¹, demonstrating the hydrous feature. After the thermal treatment, the broad peak is almost disappeared, indicating the successful dehydration of the evacuated Ni-BHC.

Figure 3c shows the XRD patterns of the well-ground Ni-BHC, consistent with the simulated results. The (200) peak at 10.364° corresponds well with the interlamellar spacing of 8.5285 Å (a/2). Generally, removing a large amount of coordinated solvent molecules will degrade the crystallinity of MOF, thus giving an amorphous XRD pattern.^{21,23,27,28} However, the Ni-BHC structure can be re-established upon soaking in water for one day, as illustrated in Scheme S1. Hence, we believe that the coordination network of evacuated Ni-BHC, mainly metal oxygen coordination bond, is retained at molecular level after the thermal treatment process.²⁴ Furthermore, the morphology of the evacuated Ni-BHC is quite similar to that of the fresh Ni-BHC, as displayed in Figure S3, supporting the reversibility of dehydration.

DFT Calculation. To evaluate the redox properties and electronic conductivities of the Ni-BHC MOFs, we calculated the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) using the DFT method with B3LYP/6-311+G(d,p). As shown in Figure 4,



Figure 3. (a) TG curves, (b) FTIR spectra, and (c) XRD patterns of Ni-BHC and evacuated Ni-BHC, respectively. The FTIR spectrum of mellitic acid is plotted in (b) for comparison. The XRD patterns of simulated Ni-BHC and re-established Ni-BHC are also displayed for reference.



Figure 4. Energy diagrams of mellitic acid, Ni-BHC, and evacuated Ni-BHC implemented in Gaussian 09w suite of program. The left axis represents the relative voltage (versus Li/Li⁺, $E_{\text{Li/Li+}}$), and the right axis represents the relative energy level in vacuum (E_{vac}). The two voltages are approximately transformed via NHE (E_{NHE}) by the following formula: $E_{\text{Li/Li+}} - 3.04 = E_{\text{NHE}} = -E_{\text{vac}} - 4.5$.

the LUMOs of Ni-BHC (-3.306 eV) and evacuated Ni-BHC (-3.789 eV) are much lower than that of mellitic acid (1.802 eV). Lower LUMO usually stands for greater electron affinities and higher redox activity with Li. So, the evacuated Ni-BHC has the highest redox activity, while the mellitic acid cannot react with

Li for its highest LUMO value. Furthermore, the gaps (ΔE)

between the HOMO and LUMO levels are closely related with

electronic conductivities, and a lower gap means good electro-

conductivity.²⁹ Thus, the high gap (6.851 eV) demonstrates an

intrinsic insulation feature of mellitic acid. It is well-documented that the conjugated carboxylate groups, as weakly electron with-

drawing ligands, can be used directly for Li storage.^{30,31} However,

the low redox activity and electroconductivity restrict its per-

formance. Due to the coordination of Ni(II) and mellitic acid

with consequent 2p-3d orbital overlap and hybridization, the

gaps are effectively reduced, suggesting the higher electronic

conductivities of Ni-BHC and evacuated Ni-BHC. It should

also be noticed that water molecules in the 3D structure can

reduce the activation energy for lithium-ion insertion; hence,

the Ni-BHC with many coordinated water molecules shows a

lower energy gap (0.541 eV) than that of evacuated Ni-BHC

(0.850 eV).^{32,33} However, the water content is quite high for Ni-BHC (~40%), which would lead to limited reversible capacity

Li-Storage Performance. A CR2032 coin-type cell config-

uration was used to evaluate the electrochemical performance

of the evacuated Ni-BHC. The cycle performance was measured

at 100 mA g^{-1} , as displayed in Figure 5a. The evacuated Ni-BHC

displays an initial discharge and charge capacity of 2114.5 and

1568.4 mA h g^{-1} , maintaining a Coulombic efficiency of 74.17%.

While the Ni-BHC and mellitic acid possessed only initial discharge capacities of 1398.7 and 135.8 mA h g^{-1} , far below that

of evacuated Ni-BHC. The evacuated Ni-BHC displayed a

capacity of 1664.4 mA h g^{-1} after 5 cycles and a capacity of 1261.3 mA h g^{-1} after 50 cycles. By contrast, Ni-BHC and mel-

litic acid maintained a low reversible capacity of only 910.4 and

and large amount of side reactions.



Figure 5. (a) Cyclic performance of evacuated Ni-BHC at a current density of 100 mA g^{-1} . The discharge curves of mellitic acid and Ni-BHC are also provided for comparison. (b) Rate performance of the evacuated Ni-BHC at different current densities ranging from 100 to 5000 mA g^{-1} . (c) CV curves at different scan rates of the evacuated Ni-BHC. (d) log *i* vs log *v* plots at different oxidation and reduction states of evacuated Ni-BHC.





82.6 mA h g⁻¹ after 50 cycles. It should be noted that supposing that this system could absorb 30 Li ions, the evacuated Ni-BHC could reach a high theoretical capacity of 1570 mA h g⁻¹, while the Ni-BHC could maintain a low theoretical capacity of only 961 mA h g⁻¹. The initial two discharge/charge profiles plotted in Figure S4 also declare their different performances. The overall performances of the three materials are quite in line with our forecast, showing the alluring promise of designing functional MOFs with luxuriant carboxylate—metal units as high performance LIB anode. Furthermore, the reversible capacity of 1261.3 mA h g⁻¹ outperforms all the other MOF anodes reported to date as far as we know (Figure 6).

To further investigate the high power performance of the evacuated Ni-BHC, rate capability was evaluated from 100 to 200, 500, 1000, 2000, and 5000 mA g^{-1} , as plotted in Figure 5b.

The discharge capacities corresponding to these current densities are 1563.1, 1437.2, 1215.1, 983.6, 740.8, and 422.0 mA h g⁻¹, respectively. After the rate test, the capacity could recover to 1293.0 at 100 mA g⁻¹, demonstrating excellent rate performance. Figure S5 shows the corresponding rate profiles of the evacuated Ni-BHC. It should be noticed that there is no plateau in the profiles, indicating a capacitive-controlled electrochemical behavior. To measure this behavior, CV measurements were performed at various sweep rates (from 0.2 to 1.2 mV s⁻¹), as displayed in Figure 5c. The capacitive effect of the electrode can be described by the following equation:

$$i = av^{\nu}, \log i = b\log \nu + \log a$$

(where *i* is the measured peak current, v is the scan rate, and *a* and *b* are adjustable parameters). It is well-known that for a

Inorganic Chemistry

diffusion-controlled Faradaic process, b approaches 0.5, while for a surface-controlled capacitive process, b is close to 1.0. In this case, as displayed in Figure 5d, the *b*-values for the 4 oxidation and reduction CV peaks are 1.046, 0.906, 0.817, and 0.680, respectively. The high *b*-values, especially for cathodic peaks, demonstrate the ultrahigh capacitive contribution (in some cases, we use the word pseudocapacitance) in evacuated Ni-BHC. Such a capacitive behavior can be attributed to the layered fastkinetics structure which will notably increase the diffusion rate of Li ions inside the bulk MOF.

Lithiation–Delithiation Mechanism Investigation. To demonstrate the participation of carboxylate groups during the electrochemical process, synchrotron-based soft X-ray total electron yield (TEY) spectra at O K-edge were also done for the evacuated Ni-BHC electrode discharged and recharged to the desired states-of-charge (SOC). As Figure 7 shows, the pre-edge



Figure 7. O K-edge sXAS TEY spectra of the evacuated Ni-BHC discharged or recharged to different states-of-charge at the first cycle.

region between 530 and 537 eV corresponds to the electron excitation from O 1s to the Ni 3d-O 2p hybrid orbitals, while the two broad peaks at 539.0 and 539.8 eV represent the electron excitation from O 1s to Ni 4sp-O 2p hybrid orbitals. The local environment evolution including Li-ion insertion and valence transition of coordinated metals will significantly change the strength and length of the Ni-O coordination bonds, thus influencing the needed energy for electron excitation in sXAS analysis. The Ni 3d-O 2p peak of the pristine electrode appears at 533.8 eV, while the peak moves down to 533.5 eV after discharging to 0.9 V, demonstrating the charge compensation participation of carboxylate oxygen. After discharging to 0.01 V, the Ni 3d-O 2p peak further moves to 533.2 eV, corresponding to more Li-ions adsorption by the carboxylate-metal units and further possible reduction of Ni(II) to Ni(0).15-17 The Ni 3d-O 2p peak returns to 533.5 and 533.8 eV after charging to 1.7 and 3.0 V, respectively, demonstrating reversibility of the local coordination environments upon discharge/charge process.

CONCLUSIONS

In summary, a hexacarboxylate-based layered MOF $[Ni_2(H_2O)_{10}]$ - $[Ni(H_2O)_2(C_{12}O_{12})]\cdot 6H_2O$ (Ni-BHC) was synthesized. After dehydration by thermal treatment, this MOF with abundant carboxylate groups was applied as an anode for Li storage, exhibiting a superior reversible capacity of 1261.3 mA h g⁻¹ at a rate of 100 mA g⁻¹. To our knowledge, such reversible capacity is the highest one ever reported for MOF-based materials. DFT calculation and O K-edge soft X-ray absorption spectroscopy

suggest that the luxuriant carboxylate—metal units play an important part in the electrochemical process. More work to improve the cycling stability is still in progress. Our work develops a new method to improve the energy density of MOFs by increasing the content of carboxylate groups within a proper topology choice.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b02939.

Supplementary optical micrograph, the reported MOF and CP materials for the LIB anode, XRD patterns, evacuated and re-established processes, SEM micrographs, charge–discharge profiles, and CV curves (PDF)

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The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by National Natural Science Foundation of China for Excellent Young Scholars (Grant 21522303) and National Natural Science Foundation of China (Grant 21373086 and 21703068), National High Technology Research and Development Program of China (Grant 2014AA123401), and National Key Basic Research Program of China (Grant 2013CB921800). We also acknowledge the sXAS experiments support from Shanghai Synchrotron Radiation Facility (BL08UA).

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