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One-pot synthesis of a metal–organic framework as an anode for Li-ion batteries with improved capacity and cycling stability

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ABSTRACT

Metal–organic framework is a kind of novel electrode materials for lithium ion batteries. Here, a 3D metal–organic framework $Co_2(OH)_2BDC$ (BDC = 1,4-benzenedicarboxylate) was synthesized for the first time by the reaction of Co^{2+} with a bio-inspired renewable organic ligand 1,4-benzenedicarboxylic acid through a solvothermal method. As an anode material for lithium ion batteries, this material exhibited an excellent cyclic stability as well as a large reversible capacity of ca. 650 mA h g^{-1} at a current density of 50 mA g^{-1} after 100 cycles within the voltage range of 0.02–3.0 V, higher than that of other BDC based anode.

1. Introduction

Metal–organic frameworks (MOFs) have evoked tremendous attention in the past few decades due to their intriguing structural diversities and widely potential applications on catalysis [1–3], luminescence [4,5], magnetism [6,7], non-linear optics [8], gas storage [9–12] and separation [13–15]. Recently, some of the research works have been focused on the design and synthesis of MOFs for clean energy applications, such as fuel cells, lithium ion rechargeable batteries, supercapacitors and solar cells [16–18]. Especially, MOFs have emerged as novel electrode materials with considerable promise in lithium ion batteries, owning to their structural diversity, tunable redox properties, simple synthetic processes and low cost.

Tarascon et al. have done pioneering work on the use of MOFs as electrode materials for lithium ion batteries. They discovered the first cathode material MIL-53(Fe) with the gravimetric capacity of 75 mA h g^{-1} [19]. In addition, they reported $Li_2C_8H_4O_4$ (Li terephthalate) and $Li_2C_6H_4O_4$ (Li *trans-trans*-muconate) as anode materials with initial capacities of 300 and 150 mA h g^{-1}, and discharge capacities remained at 78% and 74% of their initial capacities after 50 and 80 cycles, respectively [20]. Following this idea, many attempts on exploring novel MOFs electrode materials have been carried out and a series of lithium-organic coordination compounds, such as $[Li_2(C_6H_2O_4)]$ [21], $[Li_2(C_{14}H_6O_4)]$ [22], $[Li_4(C_6O_6)]$ [23], $Li_4C_{24}H_8O_8$ [24] have been investigated as electrode materials for lithium ion batteries. However, the electrochemical properties including capacities, cycleabilities and rate capabilities need to be further improved for these MOF materials. In 2010, a series of formate based MOFs $Zn_3(HCOO)_6$, $Co_3(HCOO)_6$ and $Zn_{1.5}Co_{1.5}(HCOO)_6$ were used as anodes for lithium ion storage through conversion reaction at low potential, the capacities of these compounds maintained at 560, 410 and 510 mA h g^{-1} after 60 cycles, respectively [25]. More recently, Sun et al. reported two metal–organic hybrid compounds based on 1,4,5,8-naphthalenetetracarboxylates (NTC) ligand, namely, Li-NTC and Ni-NTC [26], in which Li-NTC showed better electrochemical properties than that of Ni-NTC with discharge and charge capacities of 468 and 458 mA h g^{-1} after 80 cycles, respectively. Therefore, it is a promising and challenging work on the design and synthesis of novel MOFs for lithium ion batteries.

In order to develop novel MOF electrode materials, we focus our attention on 1,4-benzenedicarboxylate (refered as BDC in the following text) based MOFs because 1,4-benzenedicarboxylic acid, as a classic ligand has constructed a series of metal–organic architectures that could provide us candidates for the development of electrode materials [27–29]. More importantly, 1,4-benzenedicarboxylic acid, as a starting material, is available in abundance from the recycling of polyethylene terephthalate and the metabolites of aromatic hydrocarbon oxidation, meeting the requirements of future large scale applications [19]. Among these 1,4-benzenedicarboxylate based MOFs, a 3D framework, namely, $Co_2(OH)_2BDC$ attracts our attention which was first synthesized

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by Kurmoo et al. and investigated as a molecular metamagnet with a complex magnetic structure in the year of [30]. The structure of the framework consists of two types of edge-sharing CoO_6 chains that are connected to each other by the μ^3-OH to form layers that are further linked together by terephthalate bridges. Herein, we demonstrated a convenient one-pot solvothermal method to obtain this material with good purity and crystallinity and explored the possible application of this material as an anode for lithium ion batteries.

2. Experimental

$Co_2(OH)_2BDC$ was solvothermally synthesized by reacting $Co(NO_3)_2 \cdot 6H_2O$ (0.375 g, 1.289 mmol) with 1,4-benzenedicarboxylic acid (H_2BDC) (0.105 g, 0.632 mmol) in a mixture of DMF, absolute ethanol and deionized water (60 mL, 1:1:1 V/V/V). The reaction was carried out in a 100 mL Teflon-lined autoclave at 110 °C for 2.75 days. The reddish–orange products were filtered off, washed with hot ethanol, and dried at ambient temperature. Anal. Calcd (%) for $Co_2O_6C_8H_6$: C, 30.41; H, 1.91. Co, 37.3 Found (%): C, 30.37; H, 1.71, Co 36.9; FTIR in KBr disk (ν/cm^{-1}) 3600(m), 1589(vs), 1499 (m), 1363(vs), 1145(w), 1100(m), 1015(w), 813(s), 745(s), 692(m), 519(w), 462(m).

The elemental analysis (EA) data for C, H, N were obtained from a Vario EL III elemental analyzer. The content of Co was determined by an IRIS ICP spectrograph. The powder X-ray diffraction (PXRD) patterns were obtained by a Bruker D8 Advance diffractometer with Cu*K*α radiation (λ=1.54056 Å). The refined crystal lattice parameters were calculated by the FULLPROF program. Infrared spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Bruker TENSOR 27 spectrometer. The morphology of the sample was observed by a scanning electron microscope using a Hitachi S-4800.

Electrochemical tests were carried out using coin-type cells (size: 2025), which consisted of a working electrode and a lithium foil counter electrode separated by a Celgard 2400 micro-porous membrane. The working electrodes were prepared with active materials, carbon black (super P) and poly vinylidene difluoride (PVDF) dissolved in *N*-methyl pyrrolidinone (NMP) at a weight ratio of 70:20:10. The obtained slurry was casted on the Cu foil and dried in vacuum at 100 °C for 10 h. The cell assembly was performed in an argon-filled glove box. The electrolyte used consisted of 1 M $LiPF_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio of 1:1. The cyclic voltammograms (CVs) of the $Co_2(OH)_2BDC$ electrode were conducted on coin-type cells in a voltage range of 0.02–3 V (vs. Li/Li$^+$) at a scan rate of 0.3 mV s^{-1}. All the CV measurements were carried out and recorded on an electrochemical workstation (VersaSTAT3, Princeton applied research). The electrochemical performances were measured galvanostatically at various current densities (50, 100, 250, 500 mA g^{-1}, respectively) in a voltage range of 0.02–3 V at room temperature on a Land BT2001A battery test system (Wuhan Jinluo Co., Ltd., China).

3. Results and discussion

3.1. Synthesis and characterization

$Co_2(OH)_2BDC$ has been synthesized by Kurmoo et al. employing three different solution chemistry methods [30]. However, due to the insolubility of terephthalic acid and its salt, the synthesis should be carried out in dilute solution and the product is not well-crystallized. We obtained $Co_2(OH)_2BDC$ with good purity and crystallinity through a solvothermal process by adjusting the proportion of the solvents. We found that solvents have a great effect on the purity of the products. The synthesized materials possess relatively high purity in a mixture of deionized water, DMF and absolute ethanol. By contrast, impurities were detected in the XRD analysis of the resultant materials synthesized in the absence of deionized water. Fig. 1 shows the PXRD pattern of samples synthesized at 110 °C in a mixed solution of deionized water, DMF and absolute ethanol. All the diffraction peaks are consistent with the literature [30], and no any impurities were detected in the PXRD pattern, indicating the formation of pure products which were further confirmed by an elemental content analysis. The sharp and strong diffraction peaks also confirm the well-crystallization of the products. The diffraction peaks for $Co_2(OH)_2BDC$ could be indexed to the monoclinic system with a space group *C*2/*m*, and the lattice parameters were calculated as follows: a=20.0122(5) Å, b=3.28279(8) Å, c=6.3303(7) Å, β=96.3008(7)°, V=413.367 Å^3 and D_{calc}=2.5397 g cm^{-3}. The morphology of as-synthesized products was investigated by SEM as shown in Fig. 2, which suggests that a large quantity of microcrystals has a rectangular-parallelepiped shape, confirming the well-crystallinity. However, these microcrystals aggregated together into large bulk grains. The composition of the compound was also determined by IR analyses. From the IR spectra, as shown in Fig. 3, the sharp absorption band at ca. 3600 cm^{-1} is attributed to the vibrations of hydroxide. The absence of the characteristic bands at around 1700 cm^{-1} attributed to the protonated carboxylic group indicates the complete deprotonation of BDC.

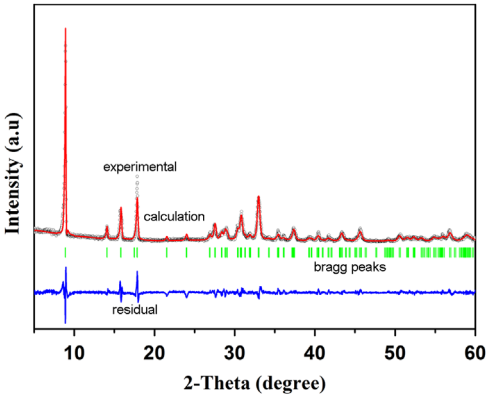

Fig. 1. The PXRD pattern of $Co_2(OH)_2BDC$ and refinement in the space group *C*2/*m*.

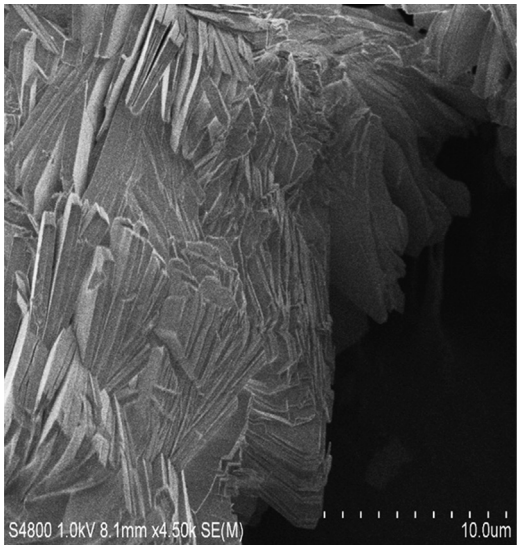

Fig. 2. The SEM image of $Co_2(OH)_2BDC$ synthesized through solvothermal process.