



Research Paper

Cobalt(II) dicarboxylate-based metal-organic framework for long-cycling and high-rate potassium-ion battery anode



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ABSTRACT

Metal-organic frameworks (MOFs) are promising electrical storage materials due to their abundant electroactive components and large ion diffusion tunnels, however, there is no report on the employment of MOFs as electrodes for potassium-ion batteries (PIBs) hitherto. Here in this work, we firstly develop a cobalt(II) terephthalate-based layered MOF (referred as 'L-Co₂(OH)₂BDC', BDC = 1,4-benzenedicarboxylate) as an anode material for PIBs. The exceptional potassium storage performance of L-Co₂(OH)₂BDC is demonstrated with a high reversible capacity of 188 mAh g⁻¹ after 600 prolonged cycles at 1 A g⁻¹, revealing the considerable foreground of MOFs as superior potassium storage anodes. Moreover, the redox chemistry investigation of L-Co₂(OH)₂BDC based on X-ray absorption near edge structure (XANES) and soft X-ray spectroscopy (sXAS) techniques substantiate that both Co centers and organic ligands participate in the potassium storage, and the coordination between oxygen ions and cobalt significantly ensures the reversibility of potassiation and depotassiation processes. This work represents a significant step forward for the intensive application of MOFs in rechargeable metal batteries.

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1. Introduction

Potassium-ion batteries (PIBs) have recently galvanized paramount attempts as one of the most promising alternatives to lithium-ion batteries (LIBs) for stationary energy storage, since K resources are much more ubiquitous and abundant in the crust of the Earth than the Li ones (2.09 wt% vs. 0.0017 wt%) [1,2]. Simultaneously, the redox potential of K⁺/K in aqueous media (-2.93 V vs. SHE) is much lower than that of Na⁺/Na (-2.71 V vs. SHE) but closer to that of Li⁺/Li (-3.04 V vs. SHE) [3–5]. Hence, PIBs have alluring potentials as low-cost rechargeable batteries with high voltage and high energy density. Recently, Komaba's group reported an inexpensive high-voltage (4 V) K-ion full cell based on K_{1.75}Mn[Fe^{II}(CN)₆]_{0.93}·0.16H₂O cathode and graphite anode and proved its feasibility as high energy density battery system [6]. Nevertheless, it is still a grand challenge to design appropriate materials that can reversibly store a substantial amount of much larger K-ions (1.38 Å) in a stable and fast manner. Up to now, carbonaceous materials such as graphite and hard carbon [7–12], alloy materials such as Sb/C, Sn/C and Sn₄P₃/C [13–15], and organic

materials such as 3,4,9,10-perylene-tetracarboxylic acid-dianhydride and dipotassium terephthalate have been investigated as PIB anodes in succession [16,17]. Besides, highly reversible potassium metal cycling was also achieved for over 200 cycles by using potassium bis(fluorosulfonyl)imide (KFSI)-dimethoxyethane (DME) electrolyte recently [18]. However, most of the reports documented hitherto are still deficient to be applied in futuristic PIBs due to the limited reversible capacity and poor rate capability, as summarized in Table 1.

Metal-organic frameworks (MOFs) or coordination network compounds (CNCs) are crystalline sponge-like materials formed by the covalently stitching of metal nodes and organic building blocks [19]. On the grounds of their abundant electroactive constituents and large ion diffusion channels, MOFs are intensively evaluated as electrical storage materials in LIBs [20–23], Li-S batteries [24], and electrochemical capacitors (ECs) in recent years [25–27]. In addition, Co 2,5-thiophenedicarboxylate and [Co(L)(H₂O)]_n·2nH₂O (L = 5-aminoisophthalic acid) MOFs have also been applied in advanced Na-ion batteries recently [28,29]. However, to the best of our knowledge, there is no report on the employment of MOFs as anode for PIBs until now, and the possibility of reversible K-storage in MOFs is still unclear.

In this article, we firstly report a cobalt(II) terephthalate-based layered MOF (hereafter referred as 'L-Co₂(OH)₂BDC', BDC = 1,4-

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Table 1The comparison of electrochemical performance between L-Co₂(OH)₂BDC and other reported anode materials for PIBs.

Materials	Cyclic performance	Rate capability	Ref.
Graphite	246 mAh g ⁻¹ at 20 mA g ⁻¹ , 200 cycles		8
Hard carbon microspheres	216 mAh g ⁻¹ at 27.9 mA g ⁻¹ , 100 cycles	240, 229, and 136 mAh g ⁻¹ at 55.8, 140, and 1395 mA g ⁻¹	9
Soft carbon	~170 mAh g ⁻¹ at 558 mA g ⁻¹ , 50 cycles	264, 210, 185, and 140 mAh g ⁻¹ at 279, 279, 558, and 1395 mA g ⁻¹	10
RGO film	120 mAh g ⁻¹ at 10 mA g ⁻¹ , 100 cycles	200, 98, and 60 mAh g ⁻¹ at 5, 50, and 100 mA g ⁻¹	11
Carbon nanofibers	80 mAh g ⁻¹ at 50 mA g ⁻¹ , 20 cycles		12
Sb/C	250 mAh g ⁻¹ at 35 mA g ⁻¹ , 50 cycles		13
Sn/C	105 mAh g ⁻¹ at 25 mA g ⁻¹ , 30 cycles		14
Sn ₄ P ₃ /C	307.2 mAh g ⁻¹ at 50 mA g ⁻¹ , 50 cycles	~350, ~320, and ~210 mAh g ⁻¹ at 50, 100, and 1000 mA g ⁻¹	15
Dipotassium terephthalate	229 mAh g ⁻¹ at 200 mA g ⁻¹ , 100 cycles; 202 mAh g ⁻¹ at 500 mA g ⁻¹ , 100 cycles; 194 mAh g ⁻¹ at 1000 mA g ⁻¹ , 500 cycles	261, 249 mAh g ⁻¹ at 50, 100 mA g ⁻¹	16
3,4,9,10-perylene-tetracarboxylic acid-dianhydride	160 mAh g ⁻¹ at 10 mA g ⁻¹ , 35 cycles		17
L-Co ₂ (OH) ₂ BDC	246 mAh g ⁻¹ at 100 mA g ⁻¹ , 50 cycles; 214 mAh g ⁻¹ at 200 mA g ⁻¹ , 200 cycles; 188 mAh g ⁻¹ at 1000 mA g ⁻¹ , 600 cycles	~352, ~271, ~228, ~201, ~159, and ~131 mAh g ⁻¹ at 50, 100, 200, 300, 600, and 1000 mA g ⁻¹	This work

benzenedicarboxylate) as an anode material for K-ion coin cells. The as-fabricated L-Co₂(OH)₂BDC is able to deliver high reversible capacities of 246 and 214 mAh g⁻¹ with Coulombic efficiencies approaching 100% at 100 and 200 mA g⁻¹, respectively. More spectacularly, a high reversible capacity of 188 mAh g⁻¹ after 600 prolonged cycles is still achieved at 1 A g⁻¹, which is the best one ever reported for PIB anodes. Furthermore, the possible redox mechanism of L-Co₂(OH)₂BDC during potassiation/depotassiation process was proposed via synchrotron-based X-ray absorption near edge structure (XANES) and soft X-ray spectroscopy (sXAS) analyses, and the results unravel that both Co centers and O-containing organic ligands participate in the potassium storage. Our work demonstrated here will open up a new train of thoughts for the wide application of MOFs in various electrical storage systems.

2. Experimental section

2.1. Synthesis of L-Co₂(OH)₂BDC MOF

All chemicals and solvents were purchased from commercial suppliers and used received. The L-Co₂(OH)₂BDC MOF was fabricated through a typical solvothermal approach. Firstly, dimethylformamide (34 mL), ethanol (10 mL), and water (10 mL) were blended into a 100 mL Teflon-lined high pressure autoclave. Then, 0.75 mmol terephthalic acid (H₂BDC) (0.25 g) and 1.50 mmol CoCl₂·6H₂O (0.357 g) were added to the above solution and dissolved under ultrasonication. Afterwards, the autoclave was capped tightly and placed in an oven at 140 °C for 48 h without stirring. Finally, the resultant crystalline materials were harvested by pumping filtration and rinsed with dimethylformamide and water for 3 ~ 6 times, followed by vacuum desiccation at 110 °C for 24 h.

2.2. Materials Characterization

Scanning electron microscopy (SEM) micrographs were observed using a S-4800 (HITACHI, Japan) scanning electron microscope operated at 10 kV. Transmission electron microscopy (TEM) images were taken on a Tecnai G2 F20 electron microscope operated at 200 kV. Powder X-ray diffraction (PXRD) patterns were conducted on a Holland Panalytical PRO PW3040/60 diffractometer, with Cu-K α radiation source ($\lambda = 1.5418 \text{ \AA}$). Continuous-wave (CW) X-band EPR spectrum was performed at 2 K with a Bruker EMX plus 10/12 spectrometer, microwave power (2 mW), modulation amplitude (2 G), modulation frequency (100 kHz), sweep

time (128 s), conversion time (16 ms) and time constant (163.84 ms) were reasonably set. X-ray photoelectron spectroscopy (XPS) spectra were carried out on an ESCALAB 250Xi X-ray photoelectron spectrometer operating at 150 W, with Al-K α radiation ($h\nu = 1486.6 \text{ eV}$). Thermogravimetric analysis (TGA) was performed by a STA 449 F3 Jupiter simultaneous thermo-analyzer at a ramping rate 10 °C/min from 25 to 800 °C in air atmosphere. N₂ sorption isotherms were obtained at 77 K with an Autosorb-IQ automated gas sorption analyser, the specific surface area was calculated through Brunauer-Emmett-Teller (BET) method. Tap density was measured with a homemade tapping apparatus (Shenzhen Sannuo Co., China).

2.3. Electrochemical Measurements

CR2032 coin cells, which were assembled in an Ar-filled glove box (O₂ \leq 0.1 ppm, H₂O \leq 0.1 ppm), were used to investigate electrochemical performance of L-Co₂(OH)₂BDC MOF. The working electrodes were composed of the as-prepared L-Co₂(OH)₂BDC active materials, acetylene black, and carboxymethyl cellulose (CMC) binder in the weight ratio of 60:30:10. The loading amount of active materials was 0.8–1.2 mg cm⁻². The potassium metal was employed as both counter electrode and reference electrode. The electrolyte was made up with 1 M KPF₆ dissolved in 1, 2-dimethoxyethane (DME), and 40 μ L of electrolyte was used in each coin cell. Whatman glassy fiber (GF-D) was employed as the separator. Galvanostatic charge/discharge measurements were conducted in the voltage range of 0.20–3.00 V (vs. K⁺/K) on a LAND CT2001A battery instrument. All the specific capacities were calculated based on the mass of L-Co₂(OH)₂BDC. Cyclic voltammetry (CV) was recorded using a CHI 660a electrochemical workstation in the potential window of 0.20–3.00 V (vs. K⁺/K). Electrochemical impedance spectra (EIS) were also carried out on a CHI 660a electrochemical workstation with the frequency range of 0.01 Hz to 100 KHz.

2.4. XANES and sXAS Characterizations

Soft X-ray absorption spectroscopy (sXAS) was monitored at Shanghai Synchrotron Radiation Facility (BL08U). Total electron yield (TEY) spectra at O K-edge were recorded via detecting the electric current caused by excited electrons from the cycled L-Co₂(OH)₂BDC samples at various SOC. X-ray absorption near edge structure (XANES) spectra were monitored at Shanghai Synchrotron Radiation Facility (BL15U). The energy resolution ($\Delta E/E$) of this facility was 2×10^{-4} , and the maximum photon flux was about

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