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Cobalt(II) coordination polymers as anodes for lithium-ion batteries with enhanced capacity and cycling stability

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Coordination polymer Co-btca (H_4btca = 1,2,4,5-benzenetetracarboxylic acid) was synthesized using a simply hydrothermal method. In particular, the as-prepared Co-btca was applied as an anode material for lithium-ion battery for the first time. Single crystal X-ray diffraction results indicated that the as-prepared Co-btca displayed unique layer structure, which was beneficial to transport Li ions and electrons. Also, owing to the porous structure and appropriate specific surface area, Co-btca electrode delivered a reversible capacity of 801.3 mA h/g after 50 cycles at a current density of 200 mA/g. The reversible capacity of 773.9 mA h/g was maintained after 200 cycles at a current density of 500 mA/g, exhibiting enhanced cycle stability. It also showed improved rate performance, making it a promising anode material and a new choice for lithium-ion batteries.

1. Introduction

Lithium-ion batteries with significantly higher specific capacity, longer storage cycle and lighter weight have been considered as the most promising energy storage system for a wide variety of applications. They have already been widely applied to mobile phones, laptops, digital cameras. The key point of lithium ion batteries properties is electrode materials [1,2]. Graphite is presently used as the commercial anode material for lithium-ion batteries; however, it is limited by the theoretical capacity (~372 mA h/g) due to the formation of the intercalation compound LiC_6. Most of the electrodes of commercialized lithium ion batteries already cannot meet demand of practical applications. Therefore, exploring novel anode materials for lithium ion batteries becomes an important and urgent issue.

Coordination polymers (CPs) are building through metal-ligand coordinations or intermolecular forces (hydrogen bonds, π–π stacking, etc.) between ligands. The term coordination polymer is nebulous, as it simply signifies the extended connection of metal and ligand monomers through coordination bonds with no regard towards the final structure or morphology [3]. Porous metal-organic frameworks (MOFs), also known as porous coordination polymers (PCPs), are self-assembly by linking inorganic and organic units via well-established principles of coordination chemistry [4]. MOFs or PCPs have evoked tremendous attention, not only for their variety of architectures and interesting molecular topologies but also due to their potential application in gas storage [5], catalysts [6], energy applications [7,8]. In particular, they have exhibited improved performance in the field of lithium-ion batteries as a kind of novel electrode material [9–11]. Many researches have emerged rapidly since Chen and co-workers [12] firstly reported MOF-177 as the anode for lithium-ion batteries. Vittal et al. [13] proposed a series of MOFs containing $HCOO^-$ group for anode showing better electrochemical performance. A 3D MOF named $Co_2(OH)_2$BDC obtained a nearly invariable capacity of 650 mA h/g in 100th cycles at the current density of 50 mA/g [14]. Especially, a Ni-based MOF with obvious ion diffusion channels which could be easily observed from its crystal structure delivered a reversible capacity of 620 mA h/g at a current density of 100 mA/g after 100 cycles [15]. Furthermore, Liu et al. [16] reported a manganese-based layered coordination polymer ([Mn(tfbdc)(4,4′-bpy)$(H_2O)_2$], Mn-LCP) exhibiting an irreversible initial high discharge capacity of 1807 mA h/g and a reversible lithium storage capacity of up to about 390 mA h/g from the fourth cycle. Fei et al. [17] found a simple and

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versatile method for preparing hollow cobalt furandicarboxylate microspheres, tested as anode material for lithium-ion batteries with high discharge capacity and good cycling stability. A reversible capacity of 549.8 mA h/g yielded after 95 cycles at 100 mA/g. Hu et al. [18] synthesized bimetallic coordination polymers (BiCPs) with Zn and Co and applied for anode materials. When the rate was 100 mA/g, a capacity of 1211 mA h/g after 100 cycles could still be maintained. From the above results, it is indicated that PCPs are promising choices for novel anode materials for lithium-ion batteries. A wide variety of MOFs with interesting topological structures are likewise suggesting us that there is still more space for improvement in the field of applying PCPs as anodes for lithium-ion batteries.

Transition metal carboxylates are one of classic coordination polymers and easily prepared. 1,2,4,5-benzenetetracarboxylic acid (H_4btca) is a common and low-cost ligand for synthesizing coordination polymers. In this work, we present a facile and scalable hydrothermal method to synthesize the cobalt-based coordination polymer (Co-btca) that is used as anodes material for lithium-ion batteries for the first time. The as-prepared Co-btca displays layer structure that is beneficial for transporting Li ions and electrons. The Co-btca electrode exhibits impressive electrochemical performance in terms of high reversible capacity and remarkable cycling stability in long term cycles.

2. Experimental

2.1. Synthesis of Co-btca

All chemicals were commercially available and used as received. The Co-btca samples were synthesized via a modified method according to previous studies [19]. Typically, $Co(NO_3)_2 \cdot 6H_2O$ (1.164 g, 4 mmol) and 1,2,4,5-benzenetetracarboxylic acid (H_4btca) (0.254 g, 1 mmol) were dissolved in distilled water (20 mL), and stirred for about 30 min. The resulting solution was transferred into a Teflon-lined autoclave and heated at 130 °C for 36 h, finally cooled down to room temperature. The reddish-orange products were filtered off, washed with ethanol and distilled water, and dried at 80 °C for 12 h. The as-prepared Co-btca was used for characterization without any further activation.

2.2. Structural characterization

The crystal structure of the obtained sample was characterized by Powder X-ray diffraction (PXRD; Bruker D8 Advance, Germany) with Cu $K\alpha$ radiation (1.5418 Å) and Single Crystal X-ray Diffraction (SXRD; Bruker D8 Venture, Germany) with Mo $K\alpha$ ($\lambda = 0.71$ Å). Simulated PXRD patterns were calculated using Mercury 3.0 software with the corresponding single crystal structural data. Fourier transform infrared (FT-IR) spectra of the samples in KBr pellets were recorded using a spectrometer (Nicolet 6700, USA). Scanning electron microscopy (SEM; Quanta 200 FEI, USA) was used to characterize the morphology of the Co-btca at an accelerating voltage of 3.0 kV. Structural analysis was conducted by transmission electron microscopy (TEM; JEM-2100F, Japan). X-ray photoelectron spectroscopy (XPS) was performed on an X-ray photoelectron spectrometer (Thermo Scientific Escalab 250Xi, USA). Thermogravimetric analysis (TGA; Q600, TA, USA) was performed under N_2 atmosphere with a heating rate of 10 °C/min from 25 to 900 °C. The specific surface area of the sample was measured based on N_2 adsorption at −196 °C using the Brunauer-Emmett-Teller (BET) method (Quantachrome Autosorb iQ2, USA). The sample was degassed at 120 °C until the vacuum pressure was lower than 10^{-4} Pa. The average value of three measurements was found for each sample.

2.3. Electrochemical measurements

Electrochemical tests were carried out using 2016-type coin cells, 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 a Cu foil and dried in vacuum at 80 °C for 12 h. The cell assembly was performed in an argon-filled glovebox. The electrolyte used in this work consisted of 1 M LiPF6 in ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio of 1:1. Cyclic voltammetric (CV) and electrochemical impedance spectroscopy (EIS) were performed under an IM6 electrochemical workstation (Zahner-Elektrik, Kronach, Germany). CVs of the electrodes were conducted on coin-type cells in a voltage range of 0.01–3 V (vs. Li/Li^+) at a scan rate of 0.1 mV/s. EIS spectra recorded in the frequency between 100 kHz and 10 mHz with a perturbation amplitude of 5 mV at the open-circuit potential. The cycle and rate performances were measured by Land BT2001A battery test system (Wuhan Jinnuo Co., Ltd., China).

3. Results and discussion

3.1. Structure characterization

As seen from the coordination environment of Co^{2+} in Co-btca, the center metal Co^{2+} is six-coordinated by six O atoms (O3, O4, O5, O3#4, O4#4, O5#4) that two of them (O4, O4#4) are from two free water molecules and the other four (O3, O5, O3#4, O5#4) come from organic moieties (Fig. 1(a)). In addition, there is one type of hydrogen bond in the packing of Co-btca including O—H···O. Adjacent building blocks are connected by hydrogen bonds (O4—H4···O1; 0.65(14), 2.15(14), 2.778(6), 161(16) and O5—H5···O1; 0.5(2), 2.4(2), 2.807(10), 157.00, 1_655) to form 2D layer network (Fig. 1(b)). Such unique layer structure could provide pathways that enhance Li ions diffusion into the structure during lithium insertion/extraction so that Co-btca is expected to display favorable electrochemical properties as anodes for lithium-ion batteries.

Note that SEM show that lamellar structures are obtained, suggesting the well-crystallinity (Fig. 2(a)). Under higher magnifications, we can observe that these large bulks consist of a large quantity of agglomerated clusters, with a spheroidal shape in a densely stacking style (Fig. 2(b)). TEM images also reveal that the microstructure of the as-prepared Co-btca is agglomerated by layer and layer (Fig. 2(c, d)).

X-ray powder diffraction results of the as-prepared Co-btca and simulated are shown in Fig. 3(a). It can be seen that the observed diffraction peaks of the sample are in agreement with the simulated pattern, and no any impurities can be detected in the PXRD pattern, indicating the formation of pure products. The sharp and intensive diffraction peaks confirm the well-crystallization of the products. Fig. 3(b) shows FT-IR spectrum of the as-prepared Co-btca. The bands at ∼3424 and ∼1666 cm^{-1} could be attributed to the vibration of water[20]. The bands at ∼1585 and ∼1347 cm^{-1} are ascribed to the asymmetric and symmetric stretching vibrations for the carboxylate groups [14]. The bands at ∼1098 and ∼744 cm^{-1} represent the in plane and out C—H bending modes of the aromatic ring [21]. Consequently, the successful synthesis of single phase crystalline Co-btca can be deduced. TGA analysis (Fig. 3(c)) shows initial weight loss (∼17%) of the Co-btca occurred at 150 °C which is attributed to water loss. This indicates that Co-btca is totally stable up to 150 °C. The second weight loss (∼73%) occuring in a

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