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Zinc pyridinedicarboxylate micro-nanostructures: Promising anode materials for lithium-ion batteries with excellent cycling performance

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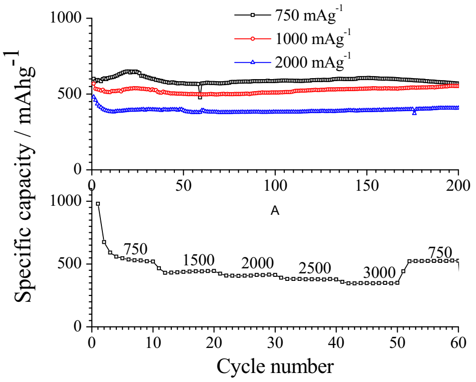
GRAPHICAL ABSTRACT



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ABSTRACT

It is important to discover new, cheap and environmental friendly coordination polymer electrode materials for lithium-ion batteries. Zinc 2,6-pyridilinedicarboxylate particles show better cycling stability and higher discharge capacity than 2,5-pyridilinedicarboxylate micro-platelets when they are firstly tested as anode materials for lithium-ion batteries. The former can steadily cycle at current densities of 750, 1000 and 2000 mA g^{-1}. It is also stable in multiple insertion/extraction processes at current densities of 750, 1500, 2000, 2500, 3000, and 750 mA g^{-1}, and the capacity retention is 77.9% after 60 cycles. While the latter is apt to show good cycling performance at smaller discharge current density.

1. Introduction

Lithium-ion battery has attracted much interest due to high energy density, long life and good rate capability [1]. Nowadays, great attentions have been drawn to develop anode materials for lithium-ion batteries with high capacity to meet the need of vehicle power supply in the future.

Conjugated dicarboxylates are promising electrode materials for lithium-ion batteries [2,3]. However, metal dicarboxylate coordination polymers beyond lithium and sodium have not attracted increasing interests in lithium-ion batteries for low capacity and bad cycling stability. Cu-dicarboxylate-based metal-organic framework $[Cu_2(C_8H_4O_4)_4]_n$ delivered a reversible capacity of

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227 mA h g^{-1} [4]. $CaC_8H_4O_4$ dicarboxylate has a discharge capacity of 399 mA h g^{-1} [5]. Manganese-based layered coordination polymer ([Mn-(tfbdc)(4,4′-bpy)(H2O)2], Mn–LCP) exhibits an irreversible high capacity in the first discharge process and a reversible lithium storage capacity of up to about 390 mA h g^{-1} from the fourth cycle [6]. $Co_2(OH)_2BDC$ (BDC¼1,4-benzenedicarboxylate) 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 mAg^{-1} after 100 cycles within the voltage range of 0.02–3.0 V, higher than that of other BDC based anode [7]. A family of transition metal–organic coordination complexes with terephthalate ligands $NiC_8H_4O_4 \cdot 4H_2O$ show reversible capacities above1100 mA h g^{-1}, attributed to transition metal reduction and subsequent excessive lithiation of the organic ligands [8]. Manganese 1,3,5-Benzenetricarboxylate Metal–Organic Framework shows high specific capacities of 694 and 400 mA h g^{-1} at current densities of 0.1 and 1.0 Ag^{-1} along with good cyclability, retention of capacity, and sustenance of the MOF network [9]. Metal formate $Zn_3(HCOO)_6$ with diamondoid structure was obtained with a discharge capacity up to 560 mA h g^{-1} (9.6 mol of Li) as with 60 cycles at a current density of 60 mAg^{-1}, which is attributed to the reversible formation or regeneration of FOR1 MOF during the cycling and electrochemical alloying-dealloying process of Zn [10].

Though transition metal polypyrrole and polythiophene coordination complex shows a high discharge capacity and good cycling stability [11–14]. Few attentions were drawn to transition metal dicarboxylate coordination polymer with heteroatom organic ring [15]. Herein, we prepared two novel zinc 2,5-pyridinedicarboxylate and 2,6-pyridinedicarboxylate coordination polymers. They were firstly found to be high-capacity anode materials for lithium-ion batteries with good cycling performance. The electrochemical property is related to the moiety of pyridinedicarboxylic acids.

2. Material and methods

All chemicals are commercially available and used as received. In a typical procedure, equal mmol 2,5-pyridinedicarboxylic acid and zinc nitrate was added to the mixed solution and stirred at room temperature for 2 h. After that, the mixture was transferred to a 50-ml Teflon-lined stainless autoclave, sealed, kept at 200 °C for 24 h, cooled to room temperature, washed with absolute alcohol and dried at 70 °C for 12 h (denoted as py25-1). When 2,6-pyridinedicarboxylic acid was used to take the place of 2,5-pyridinedicarboxylic acid. The other sample was fabricated under the identical condition (denoted as py26-1). Sample py25-2 was prepared at 180 °C for 24 h with other identical condition to that of sample py25-1. Sample py26-2 was prepared with 0.5 g polyethylene glycol under the identical condition to that of sample py26-1.

The morphological characteristics of the as-synthesized materials were observed with a Hitachi S-4800 field emission scanning electron microscope (SEM). X-ray diffraction (XRD) patterns were recorded on a diffractometer (Co Kα, PANalytical, and X'Pert). The FT-IR spectra were recorded on an America Thermo Fisher Scientific Nicolet 6700 spectrometer. A Land CT2001A battery tester was used to measure the electrode activities at room temperature. A Varo EL elemental analyzer from German Elementary Analyses System GmbH and Optima 8000 ICP-OES from American Perkin-Elmer were used for elemental analysis of H, C, N and Zn. Thermal analysis measurements were performed using a German Netzsch DIL402C Aanalyzer. X-ray photoelectron spectroscopy (XPS) measurements were performed with an Escalab 250 spectrometer. Cyclic voltammetry (CV) experiments were performed with a Chi660c electrochemical workstation at a scan rate of 1 mV S^{-1}.

The two coordination polymers were tested as anode materials for lithium-ion batteries. The composite of negative electrode material was consisted of the active material, a conductive material (super-pure carbon) and binder polyvinylidene difluoride in a weight ratio of 6/3/1. The Li metal was used as the counter electrode. The cells were charged and discharged between a 0.05 and 3.0 V voltage limit. The electrochemical impedance measurements were carried out by Zahner IM6 using a 5 mV oscillation amplitude which was applied over the frequency of 5 MHz to 0.1 Hz frequency ranges. The equivalent circuit was fitted by the Zman 2.0 software of the Zahner IM6 electrochemical workstation. The cells were discharged and charged for the first time, and then were kept at the open circuit condition for 2 h before performing impedance tests.

3. Results and discussion

X-ray diffraction was performed to identify the crystalline structure in Fig. 1. The X-ray diffraction patterns show that zinc 2,5-pyridilinedicarboxylate is crystalline (Fig. 1a). Its diffraction peaks are located at 7.82, 9.39, 10.34, 11.50, 13.82, 14.77, 15.71, 16.98, 17.18, 17.82, 18.35, 20.55, 21.29, 22.66, 23.19, 23.50, 25.71, 26.24, 26.77, 27.92, 28.87, 29.40, 30.45, 31.29, 32.14, 32.66, 33.29, 34.03, 34.77, 36.24, 37.61, 38.77, 40.24, 40.77, 41.82, 42.14, 43.51, 44.35, 44.77, 45.82, 47.40, 48.14, 49.50,

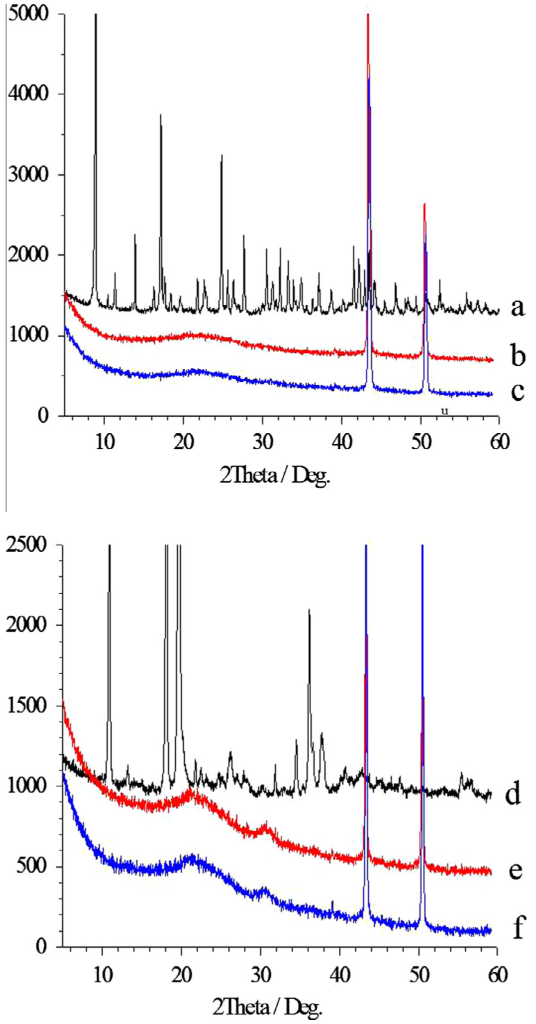

Fig. 1. Wide angle XRD patterns of (a) Zn 2,5-pyridinedicarboxylate (Sample py25-1), (d) Zn 2,6-pyridinedicarboxylate (Sample py26-1) and their first discharge and charge products (b, c) and (e, f), respectively.