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Potassium terephthalate/graphene nanocomposite as advanced anode for low-cost Na-ion batteries

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ABSTRACT

Organic carbonyl compounds are regarded as the next-generation Na-ion competitors, but the high solubility into organic electrolyte and low electronic and ion conductivity limited their large-scale application. In this study, organic terephthalate potassium (K_2TP) was newly introduced as an advanced anode for low cost Na-ion batteries. After in-situ synthesized with suitable graphene (25%wt), the as-prepared K_2TP-25G nanocomposite can exhibit remarkable specific capacity of 135 mAh g^{-1} at 1 C over 200 cycles with stable capacity retention, which is superior to reported organic anodes for Na-ion batteries. The excellent electrochemical behaviors are ascribed to its stable and spacious lattice structure, the low solubility in common organic electrolyte of K_2TP, as well as the formed K_2TP-25G nanocomposite which can efficiently enhance the electronic conductivity and shorten the Na-ion pathway. These results are of importance to look insight into new organic electrode materials design for energy storage.

1. Introduction

Li-ion batteries have been widely used among many fields, including electric vehicle, mobile phone, personal computer, et al. [1,2]. Considering the lack of lithium resource, the replacement of many secondary-ion batteries have been developed in recent years, mainly include sodium-ion (Na-ion) batteries [3], potassium-ion batteries [4], aluminum-ion batteries [5] and magnesium-ion batteries [6]. Among them, Na-ion batteries were widely investigated and recognized as the most promising candidates for large-scale energy storage due to its low cost as well as the large abundance of Na element in the earth.

Compared to the traditional inorganic electrode materials with expensive transition metals and rigid structure, the naturally abundant organic electrode compounds are environmentally friendly and sustainability which can be obtained from biomass or recyclable resources. Up to now, the reported organic electrode materials can be classified with organic polymers [7], organic radical compounds [8], organosulfur [9] and organic carbonyl compounds [10] et al. In recent years, extensive researches have been constructed on small molecular conjugated carbonyl compounds, mainly focus on improving their electrochemical property and revealing their reaction mechanisms. Unfortunately, common solubility into organic ether or ester-based electrolyte according to “like dissolves like” rule resulting in fast capacity loss limited their large-scale application [11]. Physical and chemical strategies have been employed to overcome the above issue, such as constructing kinds of organic-carbon composite [12,13], nanoparticles [14] or organic salts [15].

Recently, a typical small molecular conjugated carbonyl group based materials -sodium terephthalate (Na_2TP) [16,17] was introduced as anode materials for Na-ion batteries with a theoretical capacity of 255 mAh g^{-1}. It displayed a discharge and charge platform of 0.29 and 0.56 *V*, respectively, with remarkable cyclic performance. Interestingly, Kaduk [18] solved the structures of a series terephthalate salts, including organic lithium(Li_2TP), sodium(Na_2TP) and potassium terephthalate(K_2TP), suggesting that the replacement of different cations will significantly change the crystal structure arrangement, thus leading different ion transport way. Meanwhile, theoretical calculation and experimental details suggested that the formed metal-oxygen inorganic layer provides both Na^+ ion transport pathway and storage site, whereas the benzene or other organic layer provides electron transport pathway and redox center for organic carbonyl compounds [19]. Accordingly, it is predicted that controlling the cations for organic

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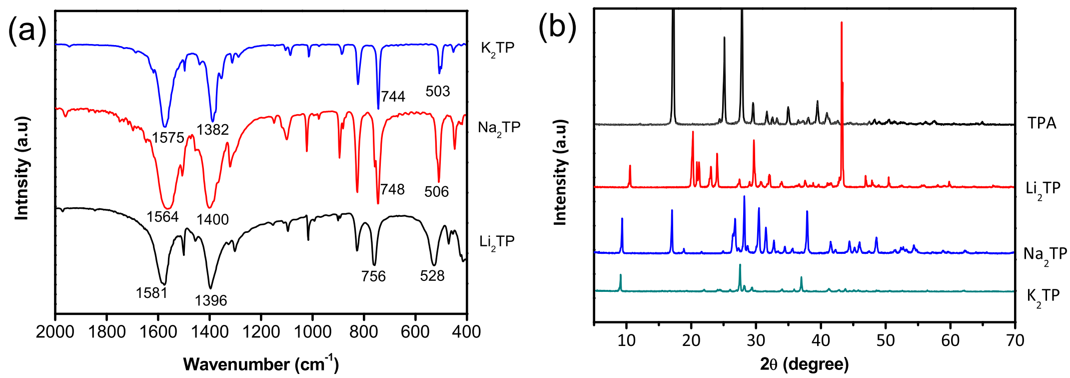

Fig. 1. (a) FT-IR spectra of Li_2TP, Na_2TP and K_2TP; (b) XRD pattern of TPA, Li_2TP, Na_2TP and K_2TP.

carbonyl compounds will significantly change the crystal structure, which can obviously affect the Na-ion and electron transport way as well as the dissolution issue in electrolyte when used as anodes for Na-ion batteries.

Inspired by the above results, herein, we proposed organic K_2TP with stable and spacious crystal structure and very low solubility in the organic electrolyte as newly anode materials for Na-ion batteries. The detailed Na storage mechanism for organic terephthalate salts is displayed in Fig. S1, which involves the breaking the C=O bond and regrouping the electrons into a set of new π-bonds during electrochemical process. K_2TP delivers cell volume decreases slightly on energy minimization and the van der Waals repulsion energy is smaller than other organic terephthalate salts. Also, the potassium cation shows the best match to the terephthalate anion than does the sodium cation for Na_2TP. The in-situ formed K_2TP-25G nanocomposite can display a reversible capacity of 135 mAh g^{-1} at 1 C over 200 cycles which is superior to reported organic anodes for Na-ion batteries. Most importantly, these results offer new insight into organic electrode materials by molecular structure controlling.

2. Experimental section

2.1. Material synthesis

Potassium terephthalate (K_2TP) microsized particle was prepared via a simple wet-chemistry methodology as we previously reported [20]. The K_2TP/graphene nanocomposite was synthesized as following: Terephthalic acid and different grapheme contents (4 wt% or 25 wt%), namely K_2TP-4G and K_2TP-25G were initially mixed in a polar aprotic solvent *N*-methyl-2-pyrrolidone (NMP) solution, and then the mixture was sonicated for 1 h. After adding equivalent KOH into the mixture, the reaction proceeded under refluxing and stirring for 24 h. Back to room temperature, the resulting products were centrifuged, washed with ethanol and then dried at 150 °C overnight. For comparison, K_2TP nanoparticles were synthesized by ball-milling with super P with the radio of 7:3.

2.2. Material characterizations

X-ray diffraction (XRD) measurement was carried out by Cu Kα radiation (λ = 1.54056 Å, X'Pert Pro MPD) with the scanning rate of 0.06° s^{-1} in the 2θ range of 5–60°. Fourier transform infrared spectrometer (FT-IR, Shimadzu, IR Prestige-21) test was operated within the wavenumber range of 400–4000 cm^{-1}, and the related pellets were prepared by thoroughly mixing ~1 wt% of the as-prepared sample with spectroscopic-grade KBr in a glove box with 99.999% Ar atmosphere. The morphology image was obtained by field-emission scanning electron microscope (FE-SEM, Hitachi, S3400N). Inductively coupled plasma (ICP) emission spectrometry (Horiba JY Ultima 2) was carried out to detect the metal cations in electrolyte.

2.3. Electrochemical measurements

Electrochemical measurements were carried out by two-electrode half cells. The working electrodes were prepared by casting the slurry onto a clean copper foil, where the slurry contained the as-prepared active material (60 wt%), acetylene carbon black (30 wt%) and poly (vinylidene fluoride) binder (PVDF, 10 wt%). The counter electrode is sodium. The electrolyte is 1 mol L^{-1} $NaPF_6$ in the mixture solvents of ethylene carbonate (EC) and dimethyl carbonate (DMC) with the volume ratio of 1:1. The separator is glass fiber. These cells were assembled in Ar-filled glove box with high purity of 99.999%. The galvanostatic cycling test was carried on a LAND facility (CT2001A, LAND electronic Co.) during the voltage window of 0.01–2 *V*. Cyclic voltammograms (CV) were tested on a CHI instrument electrochemical workstation (CHI 660C) at a scan rate of 0.1 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) measurements were performed using an electrochemical workstation (CHI 660C), and the amplitude of the alternating-current (AC) signal was 5 mV over the frequency range of 10^{-1}–10^{5} Hz.

3. Results and discussion

3.1. Microstructure characterization

From the FT-IR spectra in Fig. 1.a, The bonds at 1575 cm^{-1} and 1382 cm^{-1} were assigned to the ν_a(COOK) and ν_{as}(COOK) for K_2TP. The δ (metal–O) bonds for K_2TP, Na_2TP and Li_2TP were ascribed to 503, 506 and 528 cm^{-1}, suggesting that K_2TP gave red-shifted signal compared to carboxylate peaks of the reported Li_2TP and Na_2TP. The space group of the K_2TP crystal structure is ascribed to $P2_1/c$. K_2TP crystallizes in an monoclinic lattice where K ions are trigonal prismatically coordinated and terephthalate shows β-packing, while the space group of the Na_2TP crystal structure is $Pbc2_1$. Na_2TP crystallizes in an orthorhombic lattice where Na ions are trigonal prismatically coordinated and terephthalate shows β–packing, and Li_2TP crystallizes in a monoclinical lattice $P2_1/c$, where Li cations are tetrahedrally coordinated with γ-packing of aromatic hydrocarbons. Controlling the cations for terephthalate salts change the crystal structure, which can obviously affect the Na-ion and electron transport way as well as the dissolution issue in organic electrolyte when used as anodes for Na-ion batteries which will be discussed later (see also Table 1).

The microstructure of as-prepared microsized K_2TP, K_2TP nanoparticles, K_2TP-4G, K_2TP-25G nanocomposite were shown in Fig. 2. The bulk K_2TP showed distinctive thin-slice shape with range of 5–20 μm. To further reduce the particle size and increase the electronic conductivity, a simple in-situ one-step reaction was applied to synthesize K_2TP/graphene nanocomposite (see experimental details). To study the