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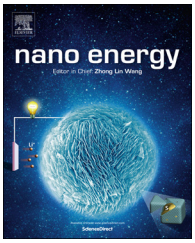

RAPID COMMUNICATION

Nanoeffects promote the electrochemical properties of organic $Na_2C_8H_4O_4$ as anode material for sodium-ion batteries

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Abstract
Recently, room temperature sodium ion batteries (SIBs) have been considered as one of the optimal alternatives for lithium ion batteries although there are still many challenges to be solved. At the present stage, the research priorities for SIBs still focus on the development of various electrode materials to meet the applicability. In this communication, we have controllably prepared a superior anode material (disodium terephthalate, $Na_2C_8H_4O_4$) with nanosheet-like morphology, which exhibits much improved electrochemical properties in terms of larger reversible capacity (248 mA h/g vs. 199 mA h/g), higher rate capabilities (for instance, 1.55 times the bulk material at 1250 mA/g) and better cycling performance (105 mA h/g vs. 60 mA h/g after 100 cycles at 250 mA/g) in comparison with the bulk one prepared at the similar system without the addition of polar solvent dimethylformamide. More importantly, it is further disclosed that, these enhanced performances could be mainly due to the new one-step desodiation mechanism and optimized ionic/electronic transfer pathways in the nanosheet system through the analyses of *ex-situ* infrared spectra, cyclic voltammogram, galvanostatic curves, scanning electron microscope images and electrochemical impedance spectroscopy.

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Introduction

Currently, lithium ion batteries (LIBs) dominate the marketplace of energy storage from portable electronic devices (such as cellular phones, laptops and personal digital assistants) to electric bicycles and vehicles [1], which might eventually lead to the shortage and price increase up to an unacceptable level of lithium resources. Therefore, it is of great significance to develop an alternative energy storage device to replace LIBs in the near future [2]. Among the extensively studied devices, room temperature sodium ion batteries (SIBs) may be an optimal choice because of its similar energy-storage mechanism to LIBs, and hence have drawn great attention due to the higher abundance and lower price of sodium resources compared to lithium ones [3-5]. However, it remains a challenging issue to obtain feasible electrode materials for SIBs with superior electrochemical properties in terms of high specific capacity, acceptable rate performance, and long cycle life, which may be mainly originated from the larger ionic radius and heavier atomic mass of sodium ions/atoms in comparison with lithium [6-9].

Although the studies of taking both Li^+ and Na^+ as charge carriers for electrochemical energy storage started at almost the same time of before 1980, significant improvements have been achieved only for LIBs in the past three decades, and it is almost disappeared to develop Na^+ accommodable materials for SIBs [10]. It is only in recent three to five years that several inorganics have been demonstrated as suitable hosts for Na^+ reversible insertion/extraction [11-16], including various metal oxides (such as spinel $Li_4Ti_5O_{12}$ anode [17,18], and layered $Na_{0.66}Li_{0.22}Ti_{0.78}O_2$ anode [19] and Na_xMnO_2 cathode [20,21]), hard carbon materials [22-25], cyan-based coordination polymers [26-28] and polyanionic compounds [29-31], One common characteristic of these materials is possessing much larger ion-transportation-channels for Na^+ accommodation and accessibility in comparison with the electrode materials of LIBs. In other words, only the inorganics with large enough ion-transportation-channels can be regarded as the potential electrode materials for SIBs, which will severely limit the diversification and development of SIBs. Fortunately, the organic electrode materials recently proposed by Armand and Tarascon [2] provide more choice and hence light the way forward for SIBs, because of their excellent adjustability by changing the functional groups, as well as structural flexibility, abundance, recyclability, low-cost and nontoxicity [13,32-36].

Amongst the organic electrode materials developed for SIBs, disodium terephthalate ($Na_2C_8H_4O_4$, Na_2TP) is one of the most promising anode candidates [37-39] due to its modest theoretic capacity of 255 mA h/g corresponding to two Na^+ insertion/extraction [37], suitable sodiation/desodiation potential versus the Na^+/Na couple as well as easy and large-scale producibility from the oxidative of low-cost paraxylene and degradation of abundant polyethylene terephthalate (PET) resin [38]. Previously, Hu [37] and Lee [38] had demonstrated respectively that Na_2TP material could store/release sodium reversibly at about 0.2–0.5 V versus Na^+/Na redox couple, which is a very suitable potential window for SIBs as anode material. In this communication, we further developed a facile solvent-induced method to successfully synthesize Na_2TP nanosheets (NS-Na_2TP), which exhibit notable nanoeffects and hence significantly promote the electrochemical properties of Na_2TP materials as anode for SIBs in comparison with bulk Na_2TP (B-Na_2TP). It is noteworthy that, the nanoeffects of organic electrode materials are still rarely studied to improve the performances of LIBs [40-42] not to be mentioned in SIBs, although it is commonplace for inorganic compounds (such as $Li_4Ti_5O_{12}$, [18] TiO_2, [43,44] sulfides, [45,46] SnO_2, [47] and so on).

Experimental section

Materials

All the materials were purchased from Beijing Chemical Reagent Factory without further purification.

Synthesis of NS-Na_2TP

The disodium terephthalate nanosheets were synthesized through a simple liquid-phase reaction with terephthalic acid as raw material. Typically, 2.52 g Aerosol OT (AOT) was dissolved in 65 mL of benzene, and then 1 mL (6 mol/L) of sodium hydroxide aqueous solution was added into the AOT benzene solution under magnetic stirring. After 30 min stirring, 5 mL (0.3 mol/L) terephthalic acid dimethylformamide (DMF) solution was added into the above solution dropwise. With 7 h magnetic stirring, the white product was obtained through centrifugation, washed several times with benzene, dimethylformamide and anhydrous ethanol in turn. Finally, the product was dried at 80 °c for 10 h in vacuum oven.

Synthesis of B-Na_2TP

The typical procedure for the synthesis of bulk disodium terephthalate was the similar to the synthesis of disodium terephthalate nanosheets as above. The difference is that terephthalic acid was added into benzene solution directly without dissolved in dimethylformamide (DMF).

Material characterization

Power X-ray diffraction (XRD) patterns were obtained from a Rigaku D/max200PC (Cu $K\alpha$ radiation), with X-ray of 40 kV and 30 mA. The Fourier transform infrared spectroscopy (FTIR) was performed with a Nicolet 6700 spectrometer from Thermo. In order to implement the *ex-situ* FTIR tests, the electrode materials containing active Na_2TP materials needed to be first scraped off from the current collector of copper foils at different charge states (pristine state, discharge to 0.01 V, and recharge to 0.5 V and 2.0 V vs. Na^+/Na) and then measured on the Nicolet 6700 spectrometer from Thermo under the ordinary procedures. The ^1H nuclear magnetic resonance (^1H NMR) spectrums were taken from a 500 MHz Superconducting NMR spectrometer (Varian INOVA 500). Scanning electron microscopy (SEM) images were from Philips XL 30 and JEOL JSM-6700F Field Emission, operated at 10 kV. Transmission electron microscopy (TEM) (JEOL-2100 F, 200 kV) was also used to character the morphology.