



Nitrogen and sulfur dual-doped carbon films as flexible free-standing anodes for Li-ion and Na-ion batteries



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ABSTRACT

Heteroatom doping is considered to be one of the most effective approaches to improve the electrochemical activity of carbon-based electrode materials for both Li-ion batteries (LIBs) and Na-ion batteries (SIBs) due to introduction of unbalanced electron atmosphere and enlarged interlayers of carbon materials. Here, we present nitrogen and sulfur dual-doped flexible carbon (NS-C) film as a promising free-standing anode for stable high-power and high-energy LIBs or SIBs. The NS-C film delivers high reversible capacities of 965.7 mAh g⁻¹ in LIBs and 520.1 mAh g⁻¹ in SIBs at a current density of 100 mA g⁻¹. Particularly, the film electrodes exhibit excellent high-rate capability and remarkable long-term cyclability. For instance, as a LIBs anode, the NS-C film remained a high capacity of 357.2 mAh g⁻¹ at 2.0 A g⁻¹ (~10 min to full charge) after 2000 cycles; even in SIBs, a capacity of 155 mAh g⁻¹ can also be reached at 1.0 A g⁻¹. It is believed that the interconnected conducting structure of carbon backbones, heteroatomic defects and increased carbon interlayers distance by stable S-C and N-C bonds are beneficial to ultrafast ion diffusion and electron transport, making the NS-C film become a high performance free-standing anode for LIBs or SIBs application.

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1. Introduction

With recent rapid development of various types of soft portable electronic equipment, such as wearable devices, artificial electronic skins and flexible touch screens, there has been an urgent market demand for thin, flexible and high-energy batteries to power them [1–4]. Among commercial rechargeable batteries, Li-ion batteries (LIBs) have the highest energy density [5–7]. For scalable deployment, however, the finite resource of lithium and high demand means that LIBs are expensive. In contrast to lithium, sodium is evenly distributed around the world and 5–7 times higher abundance than lithium [8,9]; meanwhile, sodium has a rather negative redox potential (~2.71 V vs. standard hydrogen electrode). Na-ion batteries (SIBs) are considered as one of the most promising candidates for electrochemical energy storage system after LIBs. However, the main challenge faced by SIBs is Na⁺ with around 55% larger radius than Li⁺. Therefore, how to find a suitable host material to allow reversible and rapid ion insertion and extraction is

crucial for the development of SIBs.

For achieving flexible requirements, some flexible electrodes have been developed for LIBs such as carbon nanotubes [10,11], graphene paper [12–14] and metal oxide nanowires [15,16], etc. In addition, SIBs have also attracted increasing attention for portable electronic devices in view of the more advantages of the sodium. Some researches using strategies to construct free-standing electrodes in the sodium storage for high energy purpose [17–20]. However, electron transport in these electrodes is moderate because of the relatively low quality of electronic pathway (such as chemically derived graphene), which will limit the fast charging/discharging performance. Recently we fabricated a flexible over-oxidized polypyrrole (PPy) film by a novel vapor phase polymerization (VPP) process, which was very suitable for a free-standing anode for both LIBs and SIBs due to its highly ordered and layered structure. Besides, the high electric conductive of PPy long chain structure makes the improvement of electron transport rate. Particularly, after cycling for more than 1000 times, the orderly structure of the PPy film electrode is still maintained, showing a self-adapting effect for the intercalated ions. However, the reversible discharge capacity (309.8 mAh g⁻¹ for LIBs and 215 mAh g⁻¹ for SIBs) of PPy anode is not high enough due to the nature of the

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polymers. Therefore, we further treated the PPy film by pyrolysis at a high temperature in order to obtain a carbon material to improve the charge/discharge capacities. Fortunately, the obtained carbon film keeps the continuously carbon cross-linked web sheet microstructure as the PPy precursor, which ensures good flexibility. Besides, the special molecular structure of PPy results in high N-doping level in carbon skeleton, so as to enhance the electrochemical reactivity and electronic conductivity, which additionally contributes to the exceptional electrochemical performance. As a free-standing anode for LIBs, the flexible carbon film exhibits good rate capability and cyclability [4].

Additionally, it is known that doping with large heteroatoms (such as S, or P) can increase the distances of the carbon layers, which can not only increase the migration rate of Li^+ promoting fast charge and discharge, but also improve the migration number of large Na^+ accordingly [22–25]. Besides that, the heteroatom-containing carbon functional groups can also enhance the electric conductivity by electron donors [21,23,26].

Herein we propose a modified strategy to prepare nitrogen and sulfur dual-doped flexible carbon (NS–C) films as free-standing LIBs and SIBs anodes, i.e., combining a novel vapor phase polymerization (VPP) film preparation technology with a following pyrolysis process in sulfur vapor atmosphere. The doped N and S atoms can not only influence the equilibrium state of electrons in carbon films, but also expand the interlayer distance of carbon by strong N–C and S–C chemical bonds for enhancing the Li^+ and Na^+ storage, thus the obtained NS–C film anodes show high reversible capacities together with good rate and stable cycling properties for both LIBs and SIBs.

2. Experimental section

2.1. Synthesis of PPy film precursor

PPy precursor film was synthesized by a novel vapor phase polymerization (VPP) method. Briefly, 20% Fe (III) *p*-toluenesulfonate (Sigmaaldrich) *n*-butanol solution was coated onto a glass slide substrate. After drying at 75 °C for 1.5 min, the slide was transferred to a container with full of pyrrole vapor. After 15 min, the color of the Fe (III) oxidant coating film turned to black-brown, indicating the polymerization completion. Then the polymerized PPy film can be easily peeled off from the slide by washing in ethanol solvent. The obtained PPy film was utilized as the precursor of the carbon film and the nitrogen source.

2.2. Preparation of the NS–C film

The PPy precursor film and amount of sublimed sulfur (Sigma-Aldrich) ($m_{\text{ppy}}: m_{\text{S}} = 1:1$) were encapsulated into a vacuum quartz tube, and calcined at 700 °C for 4 h with a heating rate of 5 °C min^{-1} , then cooled down naturally to room temperature. The obtained carbon based film was washed in CS_2 to remove the residual sulfur, and was named as NS–C film.

2.3. Physical characterizations

The morphologies and microstructure of the samples were characterized by a FEI Nova SEM 230 equipped with ultra-high resolution Field Emission Scanning Electron Microscope (FE-SEM) (INCA X-Max 80, Oxford Instruments), and a Transmission Electron Microscopy (TEM) (JEM-2100 F, JEOL Ltd., Japan). The X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2200/PC X-ray diffractometer at 40 kV and 20 mA, with a $\text{Cu K}\alpha$ radiation in the 2-Theta range from 10 to 80°. The Raman spectroscopies of the samples were obtained in Dispersive Raman Microscope

(Senterra R200-L, Germany). FTIR spectra were recorded on a Bruker 22 spectrometer in the frequency range of 4000–500 cm^{-1} . The surface properties of the samples were analyzed by X-ray photoelectron spectrometer (XPS, Kratos Axis Ultra DLD). The electronic conductivity of NS–C film was measured by four-point probe method (LORESTA GP, MCP-T610) at room temperature.

2.4. Electrochemical measurements

The LIB and SIB measurements were both preformed using 2032 coin cells for half-cell system at room temperature. The NS–C films were cut into round pieces with a diameter of 1.2 cm (the mass of each electrode is about 1.4 mg) by precision disc cutter machine, which were used as the electrode directly. The conducting additive and binder were not required for the electrode fabrication. The electrodes were dried in a vacuum at 80 °C for 24 h before being transferred into a glove box. The half cells were assembled in a glove box with high pure Ar. For LIBs, the coin cells were assembled with lithium metal as the counter electrode and reference electrode, and the microporous polypropylene Celgard 3501 (Celgard, LLC Corp., USA) as separator, and the electrolyte was 1.0 M LiPF_6 in a mixture of ethylene carbonate/dimethyl carbonate (EC/DEC, 1:1 v/v). For SIBs, the coin cells were assembled with sodium metal as counter and reference electrode, 1 M $\text{NaClO}_4/\text{DMC}/\text{EMC}$ (1:1:1 by volume ratio) as electrolyte. The charge and discharge performances of the half-cells were tested using a LAND CT2001A model battery test system (Wuhan Jinnuo Electronics, Ltd.) and potential was controlled between 0.01 and 3.0 V vs. Li/Li^+ or Na/Na^+ at room temperature. The cyclic voltammetry (CV) tests were performed over the potential range of 0.01–3.0 V using a Gamry Reference 6000 (Gamry Co., USA) at a scan rate of 0.1 mV s^{-1} .

3. Results and discussion

3.1. Structural and morphological features

The schematic illustration of the preparation process is shown in Fig. 1. The PPy precursor film was synthesized via a VPP bottom-up assembly method. The appointed Fe (III) tosylate oxidant could be easily spread out onto the basement such as glass slide to form a smooth oxidant film without crystallization in favor of the following homogeneous polymerization. And then the pyrrole monomers could be rapidly polymerized to PPy as soon as contacting the Fe (III) tosylate oxidant film. The macromolecular PPy chains grew along the oxidant film and then formed complete PPy films. To prepare the NS–C films, we sealed the obtained PPy film and the same weighted sublimed S into a vacuum quartz tube, and then calcined at 700 °C for 4 h to pyrolysis PPy film to carbon film and achieve N and S doping at the same time. As shown the digital images of NS–C film in Fig. 1, the NS–C film still remains the same flexible characteristic as its precursor film.

From SEM observations in Fig. 2a, the surface morphology for NS–C film presents a cross-linked net structure. The interlaced carbon net structure originates from the PPy polymer chains, which provides continuous electron channels to improve the electronic conductivity [4,21,27]. As measured by four-point probe technique, the conductivity of the NS–C film is $\sim 2.9 \text{ S cm}^{-1}$. The TEM image (Fig. 2b) shows that the NS–C film is constructed from stacked irregular multilayer carbon, which is favorable for its flexible property [28]. Notably, no obvious S bulk particles can be observed either in the SEM or in the TEM images, which may be due to the gasification of bulk S during the high temperature pyrolysis process and the sulfur gas diffusing into the pores of the carbon film by capillary force. In our previous study, it was found that the bulk sulfur can be decomposed into small sulfur molecular at a raising

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