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Novel fabrication of N-doped hierarchically porous carbon with exceptional potassium storage properties

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ABSTRACT

Potassium-ion batteries (PIBs) are an emerging energy storage technology for low cost and large scale applications. However, due to the larger K ions it suffers insufficient cycle life and poor rate capability. In this paper, these problems are surmounted by using N-doped porous carbon (NPC) anodes. Excellent electrochemical performance was demonstrated with a high reversible capacity of 296.8 mA h g^{-1} after 100 cycles at a current density of 50 mA g^{-1}. The superior performance is mainly ascribed to well-defined pore structure and high nitrogen content. The unique porous structure can effectively alleviate the volume expansion induced by the insertion of large K ions. Moreover, nitrogen doping can generate different types of defects and vacancies, thereby providing more electroactive sites. Given the abundance and universal distribution of potassium in the Earth's crust, the encouraging results make NPC a promising candidate for KIBs anodes.

1. Introduction

Nowadays rechargeable lithium-ion batteries (LIBs), as a widespread power source, have occupied the market of electrochemical energy storage fields for portable and smart electronic devices, electric vehicles (EVs), and grid-scale on account of the merits of high energy density, long cycling life and environmental benignity compared with lead-acid batteries and nickel-metal hydride batteries [1–4]. And considerable efforts have been devoted to improving performances of LIBs. However, the scarcity of Li resources, its uneven geographical distribution as well as the increasing cost have also become urgent issues to be solved, which have triggered scientists to explore renewable alternatives for energy storage and conversion. As a consequence, numerous attentions have been attracted to other novel battery systems such as sodium ion batteries (SIBs) [5–7], potassium ion batteries (PIBs) [8–10], aluminum ion batteries (AIBs) [11–13]and dual-ion batteries (DIBs) [14,15] etc.

Given the similar positions of Li, Na, and K in the periodic table and the natural abundance of potassium [16], the PIBs system could be considered as well. As potassium possesses similar physicochemical properties to lithium coupled with its pervasive distribution, PIBs exhibit promising potential for battery application. Moreover compared to SIBs, PIBs deliver a higher working voltage due to the lower redox potential of K^+/K (−2.92 V vs standard hydrogen electrode SHE) than that of Na^+/Na (−2.71 V vs SHE) [17]. Up to now, respectable capacities of K-ion electrodes have been demonstrated. Prussian blue [18,19], its analogues and $KFe^{III}Fe^{II}(CN)_6$ in both aqueous and non-aqueous electrolytes have been investigated as cathode materials of PIBs and above-mentioned materials have also displayed excellent cyclability for K-ion insertion/extraction. As we all know, graphite exhibits a reversible capacity of ~370 mA h g^{-1} by forming LiC_6, the stage-one Li−graphite intercalation compound (Li-GIC). However, the graphite, one of the most successful anodes for LIBs in commercialization, only delivers a low capacity of ~35 mA h g^{-1} by forming NaC_{64}. Surprisingly, it can form KC_8 with a remarkable capacity of ca. 273 mA h g^{-1} in PIBs [15,20–25]. Although the capacity is not pretty high and fades quickly, it still provides many new insights into electrode materials of PIBs. To date only a few anode materials (graphite [26], hard carbon [10], soft carbon [20] and Sn_4P_3/C [27]) have been studied

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because of the large size of K^+ (1.38 Å) that would give rise to sluggish reaction kinetics. Hence developing appropriate electrode materials with good performance and comprehensively investigating the mechanism are of great significance.

Carbonaceous materials, the most familiar anode materials for LIBs, are also believed as the attractive anode candidates for PIBs due to their good electrical conductivity, cost effectiveness and stable chemical and physical properties [28]. So far, lots of carbon-based anode materials have been employed for LIBs/SIBs, such as hard carbons [29], carbon nanotubes [30], carbon nanospheres [31], graphene [32] and so on. And some of them have also been utilized as anode materials in PIBs, for example, hard carbons [20], graphene [33,34]. Furthermore, carbon materials with a 3D porous structure can facilitate ion transport, especially for inner-pore ion-transport, by providing a smaller resistance and shorter diffusion pathways, which is more beneficial to electrochemical energy storage. In addition, heteroatom doping (nitrogen, phosphorus, sulfur or boron, etc.) of porous carbon materials has been proven to ameliorate electrochemical performance by adjusting the surface functional groups, enhancing the reactivity and electric conductivity [35–41]. This is principally because the formation of strong chemical bonds between the doped heteroatom and the carbon atom, which can tune the local electronic structure of porous carbon, thus influence of the electric conductivity [38–40]. Among these heteroatom elements, nitrogen doping is particularly intriguing because nitrogen has a similar atomic radius but a larger electronegativity compared to carbon, thereby leading to an enhanced interaction with potassium ions. Besides, nitrogen doping can introduce different types of defects and vacancies, and thus offer more electroactive sites. Nevertheless, high nitrogen content may influence the pore structure and electrical conductivity. Nevertheless, it still remains a challenge to build carbon nanostructures with an optimized porosity and appropriate elemental doping configuration.

Herein, nitrogen-doped porous carbon (NPC) was successfully synthesized for the first time via a facile liquid-solid absorption method followed by an annealing treatment in an inert atmosphere at 850 °C. Porous carbon with heteroatom doping improves the interface interaction and provides efficient diffusion paths for potassium ions and electrons. When applied as an anode material for the K-ion battery for the first time, the NPC presented excellent electrochemical performance, which was attributed to the synergistic effects of high nitrogen content and porous architecture.

2. Experimental section

2.1. Materials

Ammonium chloride (NH_4Cl) and sodium polyacrylate (PANa) were purchased from Sinopharm Chemical Reagent Co. Ltd. and Aladdin respectively. Unless otherwise specified, all the reagents used in this work are of analytical purity without further purification.

2.2. Preparation of N-doped porous carbon (NPC)

Specifically, 3 g ammonium chloride was dissolved in 10 mL deionized water followed by ultrasonic stirring for 10 min and then 9 g sodium polyacrylate was added into above transparent solution gradually. Subsequently 100 mL deionized water was successively poured into mixture and dried in the vacuum freeze-drying equipment to obtain a fluffy white solid. Then the solid was ground into powder, followed by heat treatment at 850 °C for 5 h at a ramp rate of 3 °C min^{-1} under an argon atmosphere. After cooling down to room temperature, the obtained product was dispersed into deionized water and stirred for 12 h to remove self-template NaCl. The mixture was washed several times until all the NaCl was removed. Finally the resultant product was vacuum freeze-dried for 12 h to obtain N-doped hierarchically porous carbon.

2.3. Material characterization

The morphologies and microstructures of the resulting materials were characterized by transmission electron microscope (TEM, JEM-2100F, JEOL, 200 kV) and field-emission scanning electron microscope (FESEM, JSM-7500F, JEOL, 5 kV). Powder X-ray diffraction (XRD) analysis was performed using a Bruker-Axs D8 Advance X-ray diffractometer with Cu Kα radiation ($\lambda = 0.15406$ nm) over the range from $2\theta = 10$ to 80°. Raman spectra were recorded on a LabRAM HR Evolution with the laser excitation of 532 nm. The electronic binding energy of the sample was examined by X-ray photoelectron spectroscopy (XPS) on ESCALab 250Xi (Thermo Scientific) instrument with Al Kα as the excitation source. Nitrogen sorption isotherms were obtained through Brunauer–Emmett–Teller (BET) analysis at 77 K on a Quantachrome Autosorb-IQ-2C-TCD-VP instrument. The electrical conductivity was measured by a Suzhou Tongchuang SZT-2A four probe resistivity tester.

2.4. Electrochemical measurements

Electrochemical performances of NPC sample as anode materials in K-ion batteries were evaluated by CR2032-type coin cells. The working electrodes were prepared by mixing the as-obtained NPC sample, carbon black and polyvinylidene fluoride (PVDF) binder to form slurry at a weight ratio of 7:2:1. N-Methyl-2-pyrrolidone (NMP) was employed to adjust the viscosity of the slurry. Then a copper foil was coated with the slurry and dried in a vacuum oven at 60 °C overnight to remove the solvent. The electrodes were punched into circular pieces with diameter of 14 mm for coin-cell testing. The circular pieces were assembled with potassium metal as counter electrode and reference electrode, glass fiber (Whatman® GF/D) membrane as a separator, and 0.8 M solution of KPF_6 in ethylene carbonate (EC) - diethyl carbonate (DEC) (1:1 v/v) as an electrolyte in an Ar-filled glove box (Mikrouna, Super 1220/750/900, $H_2O < 1$ ppm; $O_2 < 1$ ppm). Galvanostatic charge–discharge tests were performed on a LANHE CT2001A (LAND, P. R. China) in the voltage window of 0.001–3.0 V (vs. K/K^+). Cyclic voltammetry (CV) measurements were conducted on a CHI 760E at a scanning rate of 0.1 mV s^{-1} within the same potential range.

3. Results and discussion

The structures of the as-synthesized NPC samples were analyzed by X-ray diffraction (XRD) and Raman spectrum, respectively. It was observed that the as-obtained porous carbon exhibited one broad peak located at approximately 24.6°corresponding to (002) plane of the graphite microstructure, suggesting the formation of carbons with poor crystalline quality. The weaker diffraction peak located at 42.4° should be attributed to the (100) planes of graphite, confirming the existence of graphitic carbon. The interlayer distance was calculated for (002) plane and found to be 0.361 nm (Based on Bragg's equation) which is greater than 0.335 nm of pure graphitic carbon, favoring for high K ion accommodation. But the diffraction pattern of the unrinsed product displayed apparent difference, which corresponds to the crystalline NaCl (JCPDS No. 05-0628). Additionally, NaCl template has appeared before carbonization in fact and can keep relatively stable after calcination (Fig. S2). Facile self-template was generated during reaction process and can be easily removed, thereby facilitating the formation of porous morphology, which is consistent with