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Transition metal assisted synthesis of tunable pore structure carbon with high performance as sodium/lithium ion battery anode

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ABSTRACT

Template method has been used as an important method to prepare porous materials. However, there are few reports about template method employing potassium chloride as template. Here, potassium chloride is employed as a template to prepare the porous carbon, and transition metal nitrates ($Fe(NO_3)_2$,d $Co(NO_3)_2$, $Ni(NO_3)_2$) are introduced to catalyze graphitization and to result different carbon structure during carbonization (denoted as Fe@C, Co@C and Ni@C). The Fe@C shows a formicary-like structure with an about 20 nm pore diameter and the Co@C displays a completely compact structure. Whereas, the Ni@C exhibits a foam-like structure with hierarchical porous structure consisting of macroporous frameworks, mesopores and ultrathin porous walls (~5 nm). Its macropore and mesopore diameter is around 100 nm and 4 nm, respectively, its specific surface area is 464.5 $m^2\,g^{-1}$. When adopted as anode material, the Ni@C presents much outstanding rate and cycling capability for lithium and sodium storage than Fe@C and Co@C, the capacity for sodium storage is 260 mAh g^{-1} after 100 cycles at 100 mA g^{-1} and 92 mAh g^{-1} after 1000 cycles at 1A g^{-1}, and the capacity for lithium storage is 683 mAh g^{-1} after 1000 cycles at a current density of 1 A g^{-1}.

1. Introduction

Lithium ion battery (LIB) has gained much attention as a stable energy storage system because of its high energy density and high energy conversion efficiency [1–11]. For traditional LIB, the theoretical capacity of commercial graphite electrode materials is 372 mAh g^{-1}, which severely limits the improvement of energy density [12–14]. Although plenty of carbon anodes can reach a huge capacity in LIB, the complicated, environment-harmful and expensive synthesis routine remains to be improved. Sodium ion battery (SIB) is also one of the most attractive large-scale energy storage devices owing to the abundance and low cost of sodium resources [15,16]. However, the graphite cannot be used as anode and available hard carbon anode presents low specific capacity. Therefore, great efforts have been invested into carbon anode of both sodium and lithium ion battery.

Porous carbon based materials are the most promising anode for LIB and SIB due to their abundant pore structure and high specific surface area (SSA) [17–24]. Recently, many efforts have been put into the design of the carbon structure and a delightful progress has also been achieved. Porous carbon with open cellular stricture, high SSA, short ion transport distance and continuous electron pathway has been investigated as the anode materials of LIB and SIB [25–27]. To synthesize porous carbon with appropriate structure, numerous methods have been used, such as hard template, soft template, chemical/physical activation and halogen erosion method [28–32]. Soft template methods hold high controllability characteristic because of its sacrificial polymer [33]. Many researchers have synthesized porous carbon electrode using soft template method, which exhibits a good performance [34,35]. However, only few carbon precursors can meet this criterion such as phoroglucinol, resorcinol and formaldehyde. Chemical activated method and hard templates method can avoid the shortage of raw

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materials. Wang *et at.* has obtained porous carbon with good energy storage properties via carbonizing the mixture of carbonaceous species using KOH as activated agent [36]. Porous carbon was also synthesized through ordered silica as a template, which has a high specific energy capacity in LIB and SIB [28,29,37–39]. However, there still have some main drawbacks that seriously hinder their commercialization. The activated agent and erosion solution such as sodium hydroxide (NaOH), KOH or hydrofluoric acid (HF) are unavoidable for the preparation of the final product, which are normally toxic and polluted chemicals [40]. Potassium chloride (KCl), an environmental-friendly and low-cost compound, can be employed as hard template, which is easily erased by water after carbonization, and residuum keeps at a low level. The most obvious advantage is that KCl is freely soluble in water so that it can uniformly disperse in the carbon precursor solution.

Generally, porous carbon as anode of LIB and SIB possesses huge capacity, but its low conductivity and poor rate performance still seriously limits its application in high-power storage device [30,36,41,42]. Although high temperature treatment, porous carbon can be partially graphitized to improve electronic conductivity, while which would remove some Li occupied sites and result in a large capacity decrease. Thus, the high temperature treatment is not a feasible road to improve the conductivity of porous carbon [40]. Transition metal holds a high catalysis activity for the synthesis of graphite at low temperature [43]. Impregnating trace transition metal nanoparticle into carbonaceous precursor is effective way to optimize the conductivity by constructing a microcrystalline graphite conductive network.

It is worthy to employ a facial, environment-friendly and low-cost synthesis method to obtain porous carbon with desirable properties (large SSA, homogeneous architecture, high electric/ion conductivity, and appropriate porosities in micro-, meso- and macropores)In this work, the carbons with the different porous structures are tuned through adding different transition metal nitrate ($Fe(NO_3)_2$, $Co(NO_3)_2$, $Ni(NO_3)_2$) into precursor via an eco-friendly hard template synthesis routine. In this method, glucosamine is employed as precursor because of its rich resources and abundant nitrogen element, KCl acts as pore-creating agent for its water-soluble and dispersion, and trace transition metal nitrate is introduced as porous structure regulator, pore-formed agent and graphitization catalyst. Hierarchical and high graphitization porous structures with macroporous frameworks, mesopores and ultrathin porous walls (~5 nm) is obtained in Ni@C, which offers fast transport channels of ions and results in excellent rate performance. Benefiting from the unique porous structure, the obtained Ni@C shows excellent capacity (260 mAh g^{-1} in SIB), and exhibits extraordinarily good long term stability (683 mAh g^{-1} and 92 mAh g^{-1} after 1000 cycles at 1 A g^{-1} in LIB and SIB, respectively) and high rate LIB capacities as the electrode material.

2. Experimental

2.1. Synthesis of porous carbon

As is illustrated in Fig. 1, precursor was synthesized by a mild chloride template route [44]. Generally, glucosamine (2.50 g) and oxalic acid (2.5 g) was dissolved in 80 mL deionized water. Secondly, potassium chloride (8.00 g) was added as hard template and the solution became limpid uniform after 20 min stirring at room temperature. Then transition metal nitric (1.00 g) added into as-obtained solution under adequately stirring. As-mentioned limpid solution was stirred at 800 rpm min^{-1} and heated at 100 °C until mixture presented a slurry state. Then the slurry was heated to 750 °C for 4 h at a heating rate of 10 °C min^{-1} in a corundum crucible under an argon atmosphere. Finally, porous materials were obtained after deionized water and HCl washing.

2.2. Characterization

The morphology was observed via transition electron microscopy (TEM, JEOL 2010) and field-emission scanning electron microscopy (FE-SEM, Hitachi S4800) equipped with an energy dispersive spectrometer (EDS). Nitrogen adsorption and desorption isotherms were characterized using nitrogen physisorption at 77K on a Belsorp-Max/Mini system. The pore size distribution was calculated by the Barrett-Joyner-Halenda (BJH) method with the Quantachrome Instruments software. The structure was estimated by Raman spectra (LabRAM HR Evolution) and infrared spectroscopy (IR). X-ray photoelectron spectra (XPS) were collected with an ESCLab 250X.

2.3. Electrochemical measurements

The porous carbon electrode was prepared by mixing the sample (75 wt%), carbon black (10 wt%), and polyvinylidenediflouride (PVDF, 15 wt%) in N-methylpyrrolidone (NMP). The slurry was subsequently brush-coated onto copper foil, transferring electrode into a vacuum drying oven to remove the solvents. CR2032 coin cells were assembled to examine the performance of porous carbon electrode. For SIB, Na metal acts as counter electrode and 1 M $NaClO_4$ (ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 vol%) as solvent) as electrolyte. For LIB, Li metal is used as counter electrode and 1 M $LiPF_6$ with ethylene carbonate (EC)/dimethyl carbonate (DEC) (1:1 vol%) as solvent. The assembly of coin cells was carried in an argon-filled glove box. All of measurements were carried out in an atmospheric environment at room temperature, including cyclic voltammetry (CV), galvanostatic charge and discharge, and rate performance. CV measurements were tested on EC-Lab electrochemical workstation with a 0.1 mV s^{-1} scan rate from 0.01 to 2.00 V. Galvanostatic charge and discharge were carried out on a Land battery test system in the voltage ranging from 0.01 to 3.00 V. Electrochemical impedance spectroscopy (EIS) was achieved through EC-Lab electrochemical workstation with the frequency from 100 kHz to 10 MHz at room temperature.

3. Results and discussion

3.1. Structural and morphological properties

The porous carbon is synthesized by a modified potassium chloride template method. Fig. 2a, b and c present the typical SEM image of Fe@C Co@C and Ni@C, respectively. The Ni@C exhibits a foam-like structure with ultrathin pore wall and its macropores diameter are around 100 nm, the Fe@C shows a formicary-like structure with an about 20 nm pore diameter, but the Co@C displays a completely compact structure. Supplementary Fig. S1(a-i) exhibit a more clear morphology of three samples at different scales. Generally, some micromolecule becomes gas or liquid during carbonization, and is separated from parent material to form pore structure. Furthermore, plenty of pores with ultrathin carbon wall also generate after excess KCl pore-agent is erased by deionized water and the ultrathin carbon wall is favor for ion transportation. The typical TEM images of Fe@C, Co@C and Ni@C are shown in Fig. 2d, e and f, respectively. The Co@C and the Fe@C exhibit a relatively compact microstructure, but the Ni@C has abundant micropores. Otherwise it is seen that some carbon atoms layer was observed in three samples, indicating a high graphitic degree in all of the Fe@C, Co@C and Ni@C. Therefore it can be demonstrated that the Ni@C has an hierarchical pore structure