Novel nitrogen-rich porous carbon spheres as a high-performance anode material for lithium-ion batteries

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Carbonaceous materials with suitable structure and components are highly desirable for the development of lithium ion batteries (LIBs), since they can produce the best possible result by combining the advantages of the various structures and different components. To this end, herein, novel nitrogen-rich porous carbon spheres (N-PCS) with an appropriate pores distribution are proposed and prepared by using a template-assisted self-assembly method. The as-prepared N-PCS possess a high nitrogen content (>5%) and exhibit an interconnected sphere structure with large quantities of mesopores. As expected, the N-PCS display superior electrochemical performances, such as a high initial coulombic efficiency (>60%), super cycle stability (retention of 540 mA h g \(^{-1}\) after 100 cycles at 0.5 A g \(^{-1}\)), and good rate capability (215 mA h g \(^{-1}\) at 3 A g \(^{-1}\)), thereby showing great promise as anode materials for the next generation of LIBs.

Introduction

Lithium ion batteries (LIBs), as the most promising power batteries, are at the heart of technologies in developing pure electric vehicles (PEV) for their higher energy density over traditional second batteries. 1,2 Currently, graphite is the main commercial anode material, due to its low cost, long lifespan, and high initial coulombic efficiency; however, its low theoretical specific capacity (372 mA h g \(^{-1}\)) and limited rate capability make it unable to meet the ever-increasing demands of PEV. 3,4 Therefore, a lot of new materials with high energy density and rate capability, such as transition metal oxides, 5,6 lithium alloys, 7,8 non-graphite carbon materials, 9,10 and their composites, 11,12 have been studied as alternative anode materials. Among these, non-graphite carbon materials are regarded as the most promising alternative, due to their excellent cycling ability, environmental friendliness, and resource abundance.

Recently, the doping of nitrogen into the carbon crystal lattice has been proven to be an efficient approach to improve the lithium storage capacity for non-graphite carbon materials. 13–16 Cui and coworkers successfully prepared nitrogen-doped graphene nanosheets which showed a higher reversible capacity and a better rate capacity in comparison with graphene nanosheets. 13 The doping of nitrogen could increase the lithium ion adsorption energies and generate plenty of defects, which are of benefit for enhancing the lithium storage. 17–19 In addition, the presence of N atoms at the carbon surface can enhance the reactivity and electric conductivity, which favor the rate capacity. 10,11

Decreasing the transport length of lithium ions in the carbon material is another attractive approach to further improve the electrochemical performance, especially the rate capability, due to the low solid-state diffusion coefficient of lithium in the carbon materials. 20 Thus, a large number of nanocarbon materials with various microstructures have been investigated in the past five years, such as nanofibers, 10,21 nanoparticles, 22 nanosheets, 23 nanotubes, 24,25 and porous carbons. 9,26–30 Among these, porous carbons are of particular interest in providing high rate performance, because their unique structure could shorten the transport length of lithium ions and enhance the electrolyte diffusion in the carbon electrode. For instance, Song et al. prepared carbon nanosheets with different pore structures. They found that the reversible capacities increase with the increase of pore content, with the best capacity achieved being as high as 355 mA h g \(^{-1}\) at the current density of 1 A g \(^{-1}\). 28 Furthermore, to further enhance their electrochemical performance, a lot of work has been done to exploit the synergetic effect between the porous structure and the doping of nitrogen. 10,14,16 For example, mesocarbon microbead oxide (MCMB) modified by nitrogen doping has exhibited a higher reversible capacity (762 mA h g \(^{-1}\)) compared to MCMB (289 mA h g \(^{-1}\)) at the same current density. 14 Similarly, Li et al. found that a high reversible capacity of 213 mA h g \(^{-1}\), even at the rate of 3 A g \(^{-1}\), can be achieved by nitrogen-doped porous carbon. 14 In these research studies, the rate performances have shown a

\[ \text{Reaction} \]

\[ \text{Li}^+ \text{+ e}^- \rightarrow \text{Li} \]

This process is reversible, meaning that the lithium ions can be inserted and extracted from the carbon material during charging and discharging, respectively.

\[ \text{Reaction} \]

\[ \text{Li} \rightarrow \text{Li}^+ \text{+ e}^- \]

This reaction is responsible for the storage and release of electrical energy in the LIB.
great improvement by virtue of the doping of nitrogen and due to their porous structure. However, the porous structure usually contributes also to a large specific surface area, which could lead to a low initial coulombic efficiency.\cite{27,28} How to simultaneously achieve high rate capability and relatively high initial coulombic efficiency is thus still a challenge. As we know, micropores are an important contributor to the specific surface area, but could not effectively improve the electrolyte penetration and ionic diffusion in the carbon material.\cite{29,30,31,32} Therefore, it is highly possible to develop promising anode materials with high rate capability and relatively high initial coulombic efficiency by constructing new porous carbon materials, with as low an amount as possible of micropores.

Based on the above considerations, herein, we design and prepare novel nitrogen-rich porous carbon spheres (N-PCS) with an appropriate porous structure by using SiO2 as the occupying position template. The low content of micropores results in a low specific surface area, which is of benefit to enhance the initial coulombic efficiency. On the other hand, abundant mesopores were introduced to shorten the transport length of the lithium ions and facilitate liquid electrolyte diffusion. Besides, the high inherent content of nitrogen could create quantities of lithium ion storage sites and enhance the electric conductivity of amorphous carbon. Therefore, it could be expected that the N-PCS possess a relatively high initial coulombic efficiency, good rate capability, and stable cycling performance.

Experimental

Materials synthesis

All chemical reagents used in this work were analytical grade. The N-PCS were prepared using pyrrole (Py, Aladdin Industrial Corporation) as the precursor, SiO2 (Aladdin Industrial Corporation) as the template, sodium dodecyl sulfate (SDS) as the surface active agent, and FeCl3·6H2O as the initiating agent. As shown in Scheme 1, first, 0.05 g SDS and 0.2 g SiO2 were dispersed into deionized water (500 mL) by magnetic stirring for 100 min at room temperature. Then, 0.5 mL Py was added under vigorous stirring after the above solution cooled down to 0–5 °C in the refrigerator. Subsequently, 10 mL FeCl3 (0.07 mol L\textsuperscript{-1}) was added to initiate the polymerization reaction of Py. The reaction was carried out for 180 min under magnetic stirring. A black precipitate (PPy@SiO2) was obtained. The precipitate was washed with deionized water and alcohol until the filtrate became neutral. The as-prepared precipitate was thermolysised at 700 °C for 60 min under a nitrogen atmosphere. Finally, the SiO2 was removed by 10 wt% HF for 4 h with stirring. The N-PCS were obtained after washing with deionized water and drying at 80 °C in an oven for 12 h.

Materials characterization

The morphologies of the N-PCS were examined by field-emission scanning electron microscopy (SEM, Nova NanoSEM 430) and transmission electron microscopy (TEM, JEM-2010). Chemical-state analysis was carried out by X-ray photoelectron spectroscopy (XPS, ESCALAB 250). The structure was characterized by X-ray diffraction (XRD, Bruker D8 Advance) and Raman spectra (LabRAM Aramis). The BET specific surface area, pore size distribution, and total pore volume were obtained from nitrogen sorption measurements (Micromeritics analyzer ASAP 2010 (USA)).

Electrochemical measurements

The electrochemical performances of the N-PCS was tested in a half cell (CR2025) by galvanostatic cycling and by cyclic voltammetry at room temperature. The working electrodes were prepared by slurry casting on a Cu foil. The slurry contained 80 wt% active materials, 10 wt% super P, and 10 wt% polyvinylidene (PVDF) binder. The electrodes were separated by a Celgard 2325 membrane and liquid electrolyte mixtures containing 1 mol L\textsuperscript{-1} LiPF6 and a solvent mixture of ethylene carbonate (EC) and diethyl carbonate (DMC) (1 : 1 by volume) (Beijing Institute of Chemical Reagents, China). The cells were galvanostatically discharged and charged with voltages between 0.01 V and 3.0 V vs. Li/Li\textsuperscript{+} using a Battery Testing System (Neware Electronic Co., China). Cyclic voltammetry (CV) curves were measured at a scanning rate of 0.2 mV s\textsuperscript{-1}, within the potential range of 0.01–3.0 V vs. Li/Li\textsuperscript{+}, using an electrochemistry working station (Zahner IM6ex).

Results and discussion

N-PCS were prepared via the template-assisted method, as shown in Scheme 1. PPy@SiO2 nanocomposites were firstly synthesized through an in situ polymerization method, and then the PPy evolved into nitrogen-rich carbon through a thermal treatment approach. Finally, the templates were removed and the final products were obtained. The details of the fabrication are described in the Experimental section. The as-prepared product was firstly examined by Raman spectroscopy, and the pristine PPy was tested for comparison. As shown in Fig. 1a, it can be clearly seen that the characteristic peaks of PPy disappeared after a thermal treatment at 700 °C for 1 h, leaving only two peaks located at 1587 cm\textsuperscript{-1} and 1342 cm\textsuperscript{-1}, which should correspond to the graphitic band (G) and the disordered band (D), respectively.\cite{33,34,35,36} This contrastive result supports that the PPy has been successfully carbonized. In addition, it has been demonstrated that the G band is associated with the formation of sp\textsuperscript{2} carbon and the D band is associated with the disordered or imperfect structures of carbon.

![Scheme 1](Image.png)
Generally, the intensity ratio of the D band to the G band (D/G) is usually used to estimate the disorder degree of carbon. For the N-PCS, the intensity ratio of D/G is about 1.19, which is larger than other reports about amorphous carbon and close to the ratio reported for graphene materials. The result shows that the N-PCS have a higher disorder degree than other amorphous carbon. The improved disorder degree of N-PCS may be related to the precursor of the N-PCS. In detail, the nitrogen content of the PPy is more than 20% and the distribution of nitrogen atom is uniform. As a result, the inherent nitrogen atom may prevent the formation of sp² carbon and promote the growing of an imperfect structure during the carbonization process. The high disorder structure of N-PCS could be further confirmed by XRD. From Fig. 1b, it can be seen that the N-PCS have a very broad and wide peak at 24.7, which is lower than the diffraction angle of graphite, suggesting the amorphous carbon structure of the N-PCS.

To analyze the elemental composition and bonding configurations, XPS was performed on the as-prepared product. As shown in Fig. 2a, the survey spectrum of the N-PCS shows that only C, N, and O are contained and there is no peak of Si, indicating that the SiO₂ have been completely removed by HF. In addition, the result indicates that the mass percentage of doped nitrogen is as high as 5.43% of product. Fig. 2b shows the N 1s spectrum, which can be deconvoluted into three individual peaks, locating at 398.4 eV, 399.7 eV, and 400.9 eV, corresponding to pyridinic, pyrrolic, and graphitic nitrogen, respectively. The high nitrogen content in the carbon materials is beneficial to the formation of defects and the enhancement of electric conductivity, which can both enhance the electrochemical performance of the anode materials.

The microstructure of the as-prepared materials was examined by SEM, as shown in Fig. 3a; the product exhibits a spherical morphology with the diameters in the range of 50–100 nm. In addition, these nanoparticles are interconnected with each other. The morphology and structure of the as-synthesized N-PCS were further investigated by TEM. Fig. 3b shows the TEM image of the product and reveals the porous structure of the spheres. More remarkably, there is more than one pore in the sphere, which is quite different from the hollow structure sphere. Moreover, the diameters of the pores are in the range of 20–30 nm, which are equal to the diameters of the SiO₂. It is accepted that the pores are formed during the removal of SiO₂ nanoparticles. Therefore, from the above structure analysis, it is certain that interconnected nitrogen-rich carbon spheres with quantities of mesopores have been successfully prepared. The unique mesopores are ideal electrolyte diffusion channels and this interconnection feature is of benefit to electric transport, compared to the granular carbons.

To further examine the porous structure of N-PCS, the nitrogen adsorption−desorption isotherms were measured. The Brunauer–Emmett–Teller (BET) surface area of N-PCS is 67.4 m² g⁻¹. The hysteresis loops could be observed in the relative pressure of P/P₀ = 0.8–0.98 from the N₂ adsorption−desorption isotherm (Fig. 4a), which confirmed the existence of mesopores and macropores. It is acceptable that the mesopores (20–50 nm) appear during the removal of templates, which has been proven by the TEM image, and the macropores are caused by the interconnection and stacking of the carbon spheres. As reported in previous articles, the mesopores and macropores could provide ideal transport pathways for lithium ions, to improve the rate capability. In addition, the adsorption at low relative pressure (P/P₀ < 0.1) forebodes the low content of the micropores (1–2 nm). Fig. 4b shows the pore size distribution curve, showing that the as-prepared products have a low content of micropores, and quantities of mesopores and macropores. The small quantity of micropores originates from the pyrolysis process of PPy and is unavoidable in organic matter pyrolysis. The total pore volume is 0.138 cm³ g⁻¹ and the microporous volume is just 0.005 cm³ g⁻¹. The low content of micropores is beneficial to reducing the initial irreversible capacities. Therefore, N-PCS are expected to have desirable electrochemical properties.
The electrochemical performances of the as-prepared N-PCS as an anode material were investigated in a half-cell configuration at the current rate of 0.5 A g\(^{-1}\) in the voltage range of 0.01–3.0 V (vs. Li\(^+\)/Li\(^-\)). The results are presented in Fig. 5. As shown in Fig. 5a, the shape of the initial three charge–discharge cycles curves are similar to those previously reported.\(^{21,22,25}\) There is a visible broad plateau at 0.9–0.75 V in the first discharge process. However, the broad plateau at 0.9–0.75 V disappears in the following cycles. It is acceptable that the above phenomenon is due to the formation of a solid electrolyte interphase (SEI) film and other side reactions in the first discharge process.\(^{5,22}\) Notably, the initial reversible capacity is as high as 666 mA h g\(^{-1}\) at the current density of 0.5 A g\(^{-1}\), which is higher than the theoretical capacity of graphite (372 mA h g\(^{-1}\)), and also higher than those of N-carbon materials.\(^{1,16,22}\) The high reversible capacity might be related to the inherent nitrogen, which creates more Li\(^+\) storage sites. In addition, the N-PCS possess a higher content of mesopores and macropores compared to other N-carbons. The quantities of mesopores and macropores could increase the lithium storage at high potential.\(^{39}\) To further study the discharge and charge process, a cyclic voltammetry (CV) test was conducted at a scanning rate of 0.2 mV s\(^{-1}\) within the potential range of 0.01–3.0 V vs. Li/Li\(^+\). The first three cycle curves are shown in Fig. 5b. During the first cathodic scan, the N-PCS anode exhibits a cathodic peak at about 0.75 V, which may correspond to the formation of SEI film.\(^{21,41}\) In the subsequent cycles, the reduction peak at about 0.75 V disappears. The phenomenon is in good qualitative agreement with the charge–discharge cycles curves. Furthermore, the peak at above 0–0.5 V could be attributed to the lithium ion intercalating into the N-PCS. In the anodic scans, one broad oxidation peak is observed at 1.2 V, which is related to the delithiation of carbon materials.\(^{14,22}\)

Fig. 6a displays the cycling performance and coulombic efficiency of the N-PCS electrode at the current rate of 0.5 A g\(^{-1}\) in the voltage range of 0.01–3.0 V. The N-PCS electrodes show excellent cycle stability compared to other nitrogen-doped carbon nanomaterials.\(^{10,14,22}\) The initial reversible capacity is as high as 631 mA h g\(^{-1}\), but decreases fast in the following few cycles, and then the reversible capacity stabilizes. After 100 cycles, the reversible capacity is as high as 540 mA h g\(^{-1}\) and the capacity retention is 85.6% compared to the initial reversible capacity, which is indeed quite impressive. The low initial coulombic efficiency is common for amorphous carbon, and is mainly caused by the formation of the SEI film in the first discharge process.\(^{22,10}\) In our work, the initial coulombic efficiency is as high as 64%, which is higher than those of the reported N-carbons.\(^{10,14,22}\) This phenomenon may be attributed to its low specific surface area. Lower specific surface areas can usually reduce the initial irreversible capacities. Moreover, the coulombic efficiency is maintained above 99% after ten cycles, indicating the excellent cycle stability of the N-PCS. Its favorable cycle performances can be ascribed to the unique interconnected and porous structure, which provides for strain relaxation during the Li\(^+\) insertion/removal, and a suitable specific surface area, which is important for the reduction of the decomposition of electrolytes during cycling.

Besides the high cycle stability, the N-PCS also exhibit a promisingly high rate performance. Fig. 6b shows the rate capability of the N-PCS at various current densities from 0.5 to 3 A g\(^{-1}\), and then reverting back to 0.5 A g\(^{-1}\) each for 20 cycles. The reversible capacities are 542, 410, 293, and 215 mA h g\(^{-1}\) at 0.5 (1.34 C), 1 (2.69 C), 2 (5.38 C), and 3 A g\(^{-1}\) (8.06 C), respectively. The rate performance of the N-PCS electrode is excellent when compared to other reports. Zhang et al.\(^{9}\) prepared hollow carbon nanospheres, with a reversible capacity of only 229 mA h g\(^{-1}\) at the rate of 5 C. Yu et al.\(^{22}\) reported nitrogen-doped carbon nanoparticles, whose capacity is just about 300 mA h g\(^{-1}\) at the current density of 372 mA g\(^{-1}\). The super rate performance of the N-PCS anode can be attributed to the synergistic effect between its structure and its inherent high nitrogen content. More specifically, the mesoporous structure could offer a large electrode/electrolyte interface and shorten the transport length of the lithium ions, interconnected carbon nanoparticles which are beneficial to the conduction of electrons, and also the
inherent nitrogen creates more lithium ion storage sites and further enhances the electronic conductivity. All of these are important for the improvement of the rate performance of the electrode materials. When the current density is tuned back to 0.5 A g\(^{-1}\) after cycling at different rates, the specific capacity can be recovered to 570 mA h g\(^{-1}\) after 100 cycles, implying a good reversibility and high stability of the materials, which clearly benefit from its interconnected and porous structure.

Conclusion

In summary, N-PCS with appropriate pores distribution have been successfully prepared by a facile approach using SiO\(_2\) as the template and pyrrole as the precursor. The as-synthesized N-PCS used as an anode material for LIBs exhibited a large reversible lithium storage capacity (540 mA h g\(^{-1}\) in the 100th cycle at 0.5 A g\(^{-1}\)) and a superior rate capability (215 mA h g\(^{-1}\) when the discharge current increased from 0.5 A g\(^{-1}\) to 3 A g\(^{-1}\)), showing great promise as an anode material for high-performance LIBs. The super electrochemical performances originate from its unique interconnected sphere structure, appropriate pores distribution, and high inherent nitrogen content, which endow a shorter lithium-ion diffusion length and more lithium-storage sites. Furthermore, due to the high nitrogen content and the modified pore structure, N-PCS are also a potential material for application in catalysis, supercapacitors, and hydrogen storage.

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Notes and references