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Origin of extra capacity in nitrogen-doped porous carbon nanofibers for high-performance potassium ion batteries

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While graphite has limited capacity as anode materials for potassium-ion batteries, nitrogen-doped carbon materials are more promising as an extra capacity can usually be produced. However, the mechanism on the origin of the extra capacity remains largely unclear. Here, the potassium storage mechanisms have been systematically studied in freestanding and porous N-doped carbon nanofibers with an additional ~100 mAh g⁻¹ discharge capacity at 0.1 A g⁻¹. The extra capacity is generated in the whole voltage window range from 0.01 to 2 V, which corresponds to both surface/interface K-ion absorptions due to the pyridinic N and pyrrolic N induced atomic vacancies and layer-to-layer intercalation due to the effects of graphitic N. As revealed by transmission electron microscopy, the N-doped samples have a clear and enhanced K-intercalation reaction. Theoretical calculations confirmed that the micropores with pyridinic N and pyrrolic N provide extra sites to form bonds with K, resulting in the extra capacity at high voltage. The chemical absorption of K-ions occurred inside the defective graphitic layer will prompt fast diffusion of K-ions and fully realization of the intercalation capacity at low voltage. The approach of preparing N-doped carbonous materials and mechanism revealed by this work provide directions to the development of advanced materials for efficient energy storage.

Introduction

To meet the increasing energy demands, extensive efforts have been dedicated to explore green and renewable electrochemical energy storage technologies, which could lead to the substitution of traditional non-renewable energy supplies (e.g. coal, oil, natural gases, etc.).¹⁻³ Rechargeable lithium-ion batteries (LIBs), as a dominating power source, have been considered as the most promising candidates for energy storage applications.⁴, ⁵ However, the mass production of LIBs is limited due to the availability of lithium resources and the rising costs. Hence, other alkali metal ion (such as Na⁺, K⁺) batteries have attracted attention due to the abundance of Na, K and their similar chemical properties as Li.⁶, ⁷ Compared to sodium-ion batteries (SIBs), potassium-ion batteries (PIBs) have a lower redox potential (-2.93 V of PIBs vs -2.71 V of SIBs), which makes that PIBs have a higher energy density than SIBs. Moreover, owing to their large ion radius, Na⁺-ions cannot be directly intercalated into graphite which is essential for producing a commercializable anode. On the contrary, K⁺ ions can be intercalated into graphite to form potassium graphite intercalation compounds such as KₓC₆.⁸ This is an advantage for mass production in the battery industry. Hence, the research of graphitic carbons as anode for PIBs has recently been promoted. However, even the KₓC₆ at a full intercalation state has only a theoretical capacity of 279 mAh g⁻¹, and the low capacity is one of the obstacles facing the development of PIBs. Moreover, the theoretical capacity is practically hard to realize.⁹

particularly in the past decade, carbon-based materials have attracted extensive attention in energy storage because of their abundant sources, low cost, easy production and excellent chemical stability.¹⁰⁻¹² Recently, some efficient approaches have been further developed to endow novel carbon-based materials with high surface area and fast mass transport. One typical strategy is to design and construct nanostructured carbon materials to enhance the electrochemical performance for PIBs.¹³⁻¹⁵ For example, Wang et al. reported short-range order in mesoporous carbon, with a large interlayer spacing, a unique layered structure and large specific surface, thus a relatively high capacity as PIB anode of about 257.4 mA h g⁻¹ at a current density of 0.05 A g⁻¹.¹⁶ Recently, Cao et al. reported a highly graphitic carbon nanocage with a 3D electrically conducting network and highly graphitic structure. This architecture allows for a fast electron transfer and ensures a low energy and stable K⁺ intercalation/deintercalation, resulting in an excellent rate.

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capability and good cycling stability for PIB. Another important strategy is the introduction of heteroatoms (e.g., nitrogen, sulfur and phosphorus, etc.) into the carbon lattice framework, which can efficiently alter their electronic structure and thereby result in high activity for energy conversion and storage. Among these heteroatoms, nitrogen can be incorporated into the carbon framework and form strong interactions with active molecules/ions in the electrolyte due to their small size and high electronegativity. Share et al. reported nitrogen doping of few-layered graphene as anode material for PIB with a storage capacity of 350 mAh g$^{-1}$, higher than that of graphite (278 mAh g$^{-1}$). Xu et al. developed nitrogen-doped carbon nanofibers with a nitrogen content of ~13.8 wt%, exhibiting a high potassium storage capacity of 248 mAh g$^{-1}$ at 25 mA g$^{-1}$. These superior properties are mainly attributed to effects induced by the doped nitrogen. However, the detailed mechanism of nitrogen doping at the origin of this extra capacity, the electronic structure of carbon and the active/storage sites in these nitrogen-doped carbon materials still remain ambiguous due to the complexity of the nitrogen species. In the work, we tackle the mechanism by applying recent developments in both ex-situ and in-situ characterization methods to monitor the dynamical structural evolutions during the electrochemical reactions.

In addition, fabrication of freestanding and flexible nitrogen-doped carbon electrodes is highly desired in order to decrease the inactive and/or low efficient components in energy storage devices. In this regard, the development of freestanding carbon-based nanostructures without additional materials as substrates is essential to achieve cost-effective and high-performance PIBs. We report a facile and controllable method to fabricate freestanding, porous and nitrogen-doped carbon nanofibers (NCNF) by electrospinning with confinement formation of nanocrystal templates and subsequent carbonization. By modulating the amount of nanocrystal templates and heat treatment temperature, the porosity and chemical composition of the obtained NCNF samples can be easily controlled. The as-prepared sample annealed at 800°C possess a high surface area, abundant pores and high nitrogen content, and exhibits remarkable potassium storage performances. While the freestanding NCNF enable the full use of the materials as PIB electrodes, its mechanical flexibility has great potential in the application of flexible energy devices (i.e. bendable batteries). Moreover, their cycling stability is confirmed by monitoring the volumetric evolution during potassiation using in situ transmission electron microscopy (TEM). The role of doped nitrogen is studied by ex situ electron energy loss spectroscopy (EELS) and density functional theoretical (DFT) calculations. All this provides further insight into the design of functional nitrogen-doped carbon materials for energy storage.

**Experimental section**

**Synthesis of freestanding porous N-doped carbon nanofibers.**

0.4 g of Zn(NO$_3$)$_2$·6H$_2$O, 1.6 g of Zn(C$_2$H$_3$O$_2$)$_2$, 2.0 g of 2-Methylimidazole and 1.8 g of polyacrylonitrile were added in 22 mL of N,N-Dimethylformamide solution. After stirring at room temperature for 3 h, the obtained viscous and white precursor solution was electrospun at a high voltage of 10 kV and -2 kV (electrospinning equipment: SS-2534H from UCALEY Co., Beijing, China). Finally, after the composite nanowires were presintered at 220°C (3°C min$^{-1}$) in air for 1 h and annealed at 800 °C (5 °C min$^{-1}$) under argon atmosphere for 3 h, uniform porous N-doped carbon nanofibers were obtained (NCNF-800). In comparison, when the composite nanowires were presintered at 220 °C (3 °C min$^{-1}$) in air for 1 h and then treated at 1000 °C under argon atmosphere for 3 h, NCNF-1000 sample was obtained.

**Characterization.**

The crystallographic characteristics of the final products were measured using a Bruker D8 Discover X-ray diffractometer equipped with a Cu Ka radiation source. SEM images were collected using a JEOL-7100F scanning electron microscope, and TEM images were collected using a JEM-2100F/Titan G2 60-300 transmission electron microscope. STEM-EELS spectra and images were recorded using an Oxford IX300 system. XPS and UPS measurements were conducted using a VG ESCALAB 250Xi instrument. XPS and UPS measurements were conducted using an ESCALAB 250Xi instrument.

**Results and Discussion**

**Synthesis and characterization**

The synthesis procedure of freestanding porous NCNF is illustrated in Fig. S1. First, the precursor solution was prepared by mixing Zn$^{2+}$...
sources, 2-methylimidazole (2-MIM) and polyacrylonitrile (PAN) in N,N-dimethylformamide (DMF). As 2-MIM hardly deprotonates in DMF at room temperature, a viscous homogeneous solution of zeolitic imidazolate framework (ZIF) crystals is formed in the mixture. Under a strong electrostatic tension force along with the volatilization of DMF, the homogeneous solution was electrospun to form uniform precursor@PAN nanofibers. Then the precursor@PAN nanofibers are heated at 80 °C (denoted as step I). The formation of small ZIF-8 nanocrystals by the coordination reaction between zinc ions and 2-MIM as well as the crystallization of the residual 2-MIM, results in both the ZIF-8 and 2-MIM nanocrystals to be confined into the PAN nanofibers (ZIF-8&2-MIM@PAN). X-ray diffraction (XRD) patterns of ZIF-8&2-MIM@PAN nanofibers show obvious diffraction peaks from both the ZIF-8 and 2-MIM, confirming the existence of these crystals in the nanofibers (Fig. S2a, Supporting Information). As shown by scanning electron microscopy (SEM) (Fig. S2b-d, Supporting Information), the composite nanofibers have a uniform fibrous morphology with a rough surface and an average diameter of about 500 nm. Furthermore, TEM images demonstrate the existence of nanocrystals (< 50 nm in diameter) in the nanofibers (Fig. S2e and f, Supporting Information). The formed ZIF-8 and 2-MIM nanocrystals act as hard templates in the Step II process, i.e. the in situ carbonization. When the as-prepared ZIF-8&2-MIM@PAN nanofibers are treated at high temperature (> 800 °C) in argon atmosphere, the pyrolysis of confined ZIF-8 nanocrystals and the volatilization of confined 2-MIM nanocrystals, together with the carbonization of PAN result in the formation of freestanding carbon nanofibers with lots of pores with various sizes. Since N are retained in the nanofibers when the temperature is appropriate, porous NCNF are obtained. In brief, the synthesis process includes fabrication of precursor nanofibers by electrospinning, confinement formation of nanocrystal templates and in situ carbonization. By modulating the number of nanocrystal templates and the heat treatment temperature, the porosity and chemical composition in the formed NCNF can be effectively controlled as discussed below.

The morphology of the obtained NCNF has been characterized by various techniques. When treated at 800 °C, the porous NCNF (denoted as NCNF-800) show a uniform fibrous morphology with an average diameter of ~500 nm and they are assembled into a thin freestanding nanofiber film (Fig. 1a). The as-prepared films exhibit good flexibility and can directly act as a freestanding, binder-free and bendable electrode (inset of Fig. 1a). The enlarged SEM images clearly display the porous and wrinkled surface of these NCNF-800 (Fig. 1b, c). TEM images (Fig. 1d-e) indicate that the nanofibers are porous, as there are many variations in image contrast. High-resolution TEM (HRTEM) (Fig. 1f and Fig. S4a, Supporting Information) shows that the graphitic layers are curved and defective, among which encapsulated pores with a size of 5-20 nm can be seen. The pores are mainly generated by the hard template removal in annealing. The selected-area electron diffraction (SAED) patterns of the NCNF-800 nanofibers (inset of Fig. 1e) show only a weak and diffuse diffraction ring, corresponding to an interplanar distance of about 0.4 nm, which is an indication of the presence of the expanded and defected (002) graphitic lattice planes and low graphitization of NCNF-800. STEM energy-dispersive X-ray spectroscopy (STEM-EDS) mapping (Fig. 1g-i) confirms that the N is uniformly distributed in the nanofiber. Samples that underwent a heat treatment at 1000 °C will be denoted as NCNF-1000. The morphology of NCNF-1000 is similar to that of NCNF-800 as shown by the SEM images (Fig. S3, Supporting Information). However, with the increase of the treatment temperature, the surface of these samples becomes much smoother and the amount of pores decreases, which can be attributed to an increase of the graphitization degree in NCNF-1000 samples. HRTEM images (Fig. S4, Supporting Information) also show NCNF-1000 have more pronounced graphite layers than NCNF-800. The average diameter of NCNF-800 and NCNF-1000 fibers is 470 and 340 nm, respectively (Fig. S3b and e). A condense of the nanofibers takes place at the higher temperatures, leading to a smaller diameter for the NCNF-1000 nanofibers.

The structural details of both samples were further investigated by XRD, Raman and X-ray photoelectron spectroscopy (XPS) as shown in Fig. 2. The XRD patterns of the NCNF-800 and NCNF-1000 samples show only one minor diffraction peak corresponding to the expanded graphite (002) lattice planes at about 26°. The peak becomes clearer and sharpens for the NCNF-1000 sample. This confirms that the graphitization degree in the nanofibers is enhanced with increasing annealing temperature. Raman spectra exhibit two characteristic peaks from both the ZIF-8 and 2-MIM, confirming the existence of these nanocrystals in the nanofibers (Fig. S2a, Supporting Information). As shown by scanning electron microscopy (SEM) (Fig. S2b-d, Supporting Information), the composite nanofibers have a uniform fibrous morphology with a rough surface and an average diameter of about 500 nm. Furthermore, TEM images demonstrate the existence of nanocrystals (< 50 nm in diameter) in the nanofibers (Fig. S2e and f, Supporting Information). The formed ZIF-8 and 2-MIM nanocrystals act as hard templates in the Step II process, i.e. the in situ carbonization. When the as-prepared ZIF-8&2-MIM@PAN nanofibers are treated at high temperature (> 800 °C) in argon atmosphere, the pyrolysis of confined ZIF-8 nanocrystals and the volatilization of confined 2-MIM nanocrystals, together with the carbonization of PAN result in the formation of freestanding carbon nanofibers with lots of pores with various sizes. Since N are retained in the nanofibers when the temperature is appropriate, porous NCNF are obtained. In brief, the synthesis process includes fabrication of precursor nanofibers by electrospinning, confinement formation of nanocrystal templates and in situ carbonization. By modulating the number of nanocrystal templates and the heat treatment temperature, the porosity and chemical composition in the formed NCNF can be effectively controlled as discussed below.

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bonds with D band (approximately 1350 cm\(^{-1}\)) from disordered carbon and G band (~1600 cm\(^{-1}\)) from graphitic carbon (Fig. 2b). The areal intensity ratios of \(I_D/I_G\), a factor to determine the graphitization degree, are calculated to be 2.68 and 2.41 for the NCNF-800 and NCNF-1000 sample, respectively (Table S1, Supporting Information). This confirms once more that the graphitization degree of the NCNF-1000 sample, respectively. The corresponding charge and discharge voltage profiles of NCNF-800 and NCNF-1000 at different current densities. (e) Cycling performance of NCNF-800 and NCNF-1000.

The electrochemical performance of a half-cell potassium-ion battery using the as-prepared NCNF-800, NCNF-1000 samples as a freestanding binder-free anode was measured to investigate the role of the nitrogen species (Fig. 3). First, cyclic voltammograms (CVs) of the NCNF-800 and NCNF-1000 were measured in the potential range from 0.01 to 3.0 V vs. K/K\(^+\)/K at a scan rate of 0.2 mV s\(^{-1}\) (Fig. S5, Supporting Information). In the first cathodic scan of NCNF-800 and NCNF-1000, a broad peak located at 0.01-1 V can be observed, which is attributed to the formation of an SEI (Solid Electrolyte Interphase) layer.\(^{31}\) The four subsequent CV curves mostly overlap, showing a good reversibility. No obvious redox peaks appear on the fourth subsequent CV curves of the NCNF-800 due to the small size of the sp\(^2\)-domains and the discontinuous structural nature with more defective surfaces and interfaces. However, a broad anodic peak at 0.5 V and a broad cathodic peak at 0.9 V can be observed in NCNF-1000, of which the capacity mainly originates from the intercalation of K-ions into the graphitic layers (0.01-1 V).\(^{32}\) When tested at 0.1 A g\(^{-1}\), NCNF-800 shows a higher initial discharge capacity (422 mAh g\(^{-1}\)) than NCNF-1000 (345 mAh g\(^{-1}\)), indicating that there are more active sites for potassium storage in NCNF-800 (Fig. 3a). In NCNF-800, the capacity increase at initial cycles may be attributed to an increased electronic conductivity and an enhanced capability of ion-infiltration. The first Coulombic efficiency of the NCNF-800 electrode is 69.7%, which is higher than that of NCNF-1000 (52.5%). A higher ICE of NCNF-800 (than that of NCNF-100) is mainly attributed to having more reversible storage sites for K-ions, which is caused by higher nitrogen content. The rate performance was measured at different current densities ranging from 0.1 to 5 A g\(^{-1}\) (Fig. 3b). The average specific discharge capacities of NCNF-800 are 280, 260, 232, 210, 190 and 170 mAh g\(^{-1}\), respectively. However, for NCNF-1000 the corresponding specific discharge capacities are 180, 170, 157, 138, 126 and 112 mAh g\(^{-1}\). When the current density returns to 0.1 A g\(^{-1}\), the average specific discharge capacity of NCNF-800 recovers to 280 mAh g\(^{-1}\), indicating an excellent rate performance. The corresponding charge and discharge voltage profiles of NCNF-800 and NCNF-1000 are shown in Fig. 3c, d and Fig. S5. It demonstrates that in NCNF-800, besides extra capacity mainly occurring in the high potential window (from 1 to 2 V), the capacity in the low potential window (from 0.01 to 1 V) is also higher than that of NCNF-1000 (listed in Table S3, Supporting Information). In contrast, most of the capacity of the NCNF-1000 is from the low energy window range of 0.01-1 V as shown in the CV curves (Fig. S5, Supporting Information). The capacity contributions from the high voltage (above 1 V) and low voltage (below 1 V) of the discharge can be calculated at different current densities, which are in agreement with the above-analysed results (Fig. S6, Supporting Information). The long-term cycling performance of NCNF-800 and NCNF-1000 are evaluated at a high current density of 5 A g\(^{-1}\) (Fig. 3e). NCNF-800 exhibits a higher specific capacity of 150 mAh g\(^{-1}\) after 1000 cycles than NCNF-1000, showing outstanding long-term cycling stability. Furthermore, electrochemical impedance spectroscopy...
(EIS) measurements were carried out to evaluate the charge-transfer resistance ($R_{ct}$) of the NCNF-800 sample at different cycles (Fig. S9, Supporting Information). The stable and small $R_{ct}$ values of ~75 Ω at the 1$^{st}$, 10$^{th}$ and 50$^{th}$ cycle indicate that the electronic mobility is kept fast and stable during cycling. The contact resistance in PIBs is relatively low due to the good conductivity of the electrode materials and good contact between electrode materials and electrolyte. The morphological changes after 1000 cycles were studied by SEM; it shows that the overall morphology of NCNF-800 remains the same (Fig. S10, Supporting Information). The electrochemical measurements clearly demonstrate that the NCNF-800 sample has extra capacity across the whole potential range and the extra capacity is reversible (e.g. stable in charge and discharge cycles).

**In-situ TEM and ex-situ EELS Study of Electrochemical Potassiation**

To provide a more detailed insight into the potassiation process of the NCNF-800 and NCNF-1000 samples, in *situ* TEM was carried out to study the microstructural evolution in real time (Fig. 4 and 5). Both TEM images and SAED patterns were recorded during potassiation. The results reveal the following main characteristics during the potassiation process: 1) both NCNF-800 and NCNF-1000 had a negligible volume expansion during the K$^+$ insertion (Fig. 4a-c and 5a-c). The volume expansion is only about 0.5% of the NCNF-800 (diameter expands from 385.3 nm to 386.0 nm), similar to that of the NCNF-1000 (diameter expands from 507.8 nm to 508.7 nm). This is attributed to the porous structure of the NCNF, which can efficiently accommodate the volume changes and maintain structural stability in potassiation. 2) Although the overall volume expansion is quite small, the image contrast in both samples slightly changed and becomes grainy along with the potassiation, as marked by the yellow arrowheads in Fig. 4a-c and Fig. S11d-f. The varying image contrast implies the local volumetric expansion due to insertion of K. 3) The phase transformation from C to KC$_x$ due to K-intercalation is identified in both samples by dynamic SAED patterns. Before potassiation, as identified by the rings in the SAED patterns, the (002), #81, and #81) plane spacing of pristine NCNF-800 and NCNF-1000 are 4.1 Å and 3.7 Å, respectively. These spacings are slightly larger than the one of perfect graphite (3.6 Å) due to the disordered structure in NCNF (Fig. 4d). As the pristine NCNF-800 is more defective with a lower graphitization degree, its (002) lattice plane spacing is larger than that of the NCNF-1000. After complete potassiation, the (002) plane spacing of potassiated NCNF-800 increases from 4.1 to 4.3 Å, corresponding to an increment rate of around 5%. For NCNF-1000, the (002) spacing increases from 3.7 to 4.1 Å, corresponding to an increment rate of about 11%. Although the increment rates are different, the final products (e.g. KC$_x$) are the same, implying there is a similar K-ion intercalation process. Therefore, while the capacity of the highly graphitized NCNF-1000 mainly originates from an intercalation reaction, additional potassium storage capacity is also from the rich nanoropes and N-related defects in NCNF-800. 4) K has been identified by energy-dispersive X-ray spectra (EDS) mapping, which shows that K is uniformly distributed on both the potassiated NCNF-800 and NCNF-1000 samples (Fig. 4g and 5g).

The charge states of C and K in the NCNF-800 and NCNF-1000 samples, have been investigated in the pristine state as well as after the first cycle when discharged at different potentials by electron energy loss spectroscopy (EELS) as shown in Fig. 4f and 5f, to tackle their reaction mechanism. All EELS spectra were calibrated with respect to the zero-loss peak. The pristine NCNF-800 has two typical C-K edges, i.e. the π*-edge at 285.3 eV and the σ*-edge at 291.8 eV (Fig. 4f). The position of these two edges are slightly shifted to a higher energy compared to those of perfect graphite (π*-edge near 284.5 eV and σ*-edge near 290 eV). This is because the conduction band of C-atoms at defective sites have a higher energy than the ones of perfect graphite (so that the graphitic carbons have a slightly higher valence state than the ones of perfect graphite). When the PIB with NCNF-800 as anode is discharged to 1 V and beyond, the K-L edge is observed at 296 eV, confirming the insertion of K$^+$ into the NCNF-800 sample. When the PIB with NCNF-800 as anode is discharged to 1 V and even to 0.5 V, the π*-edge position of the C-K edge had no obvious shift, showing that at this stage the majority of the 2D graphitic C-atoms are still not the major host to store K+. When further discharged to 0.01 V, the π*-peak shifts to a higher energy (287.4 eV) compared with that of the pristine NCNF-800, implying a local electron transfer from K ions to the C planar π bonds. This shift can be attributed to the formation of C-K bonds, implying the intercalation reaction becomes dominant when the voltage of discharge is below 0.5 V. As for the σ*-edge (which represents the energy difference between a carbon K-shell and the σ*-conducting bond), the position shifts from 291.8 eV of the pristine NCNF-800 sample, to 292.0 eV for the 1 V-discharged sample, 292.1 eV for the 0.5 V-discharged sample and 291.4 eV for the 0.01 V-discharged sample. The shift to high energy may be caused by the formation of 3D tangling bonds between C and the adatoms such as K.

As for the pristine NCNF-1000 sample, there are two typical C-K edges located at 284.8 eV (π*-peak) and 291.8 eV (σ*-peak) in the EELS spectrum as shown in Fig. 5f. The π*-peak position is lower than that of the pristine NCNF-800 and closer to that in the perfect...
graphite crystal, which may be due to the lower nitrogen content and less C-N bonds formed in NCNF-1000. When discharged to 1 V, there is a K-L edge located near 294 eV, implying the presence of K-ion in the structure. The C π*-peak gradually shifts from 285.1 eV to 285.6 eV, finally to 286 eV, upon discharging. The continuous shift indicates that insertion of K+ directly modifies the planar framework of the π bonds as well. As for the σ*-peak, the position undergoes no obvious shift when discharged to 1 V and even to 0.5 V. However, when discharging to 0.01 V, it shifts to 292.6 eV.

The EELS studies reveal the different behavior of the C near edge peaks upon discharging. When the discharging voltage is higher than 0.5 V, the overall σ*-peak of the NCNF-800 sample is higher than that of NCNF-1000, an indication of more active sites on the surface and interfaces in the N-rich NCNF-800 sample. At a discharging voltage of 0.01 V, the N-rich NCNF-800 sample has a relatively higher local electron transfer into the C planar π bonds, because of the presence of K ions (287.4 eV), than the NCNF-1000 sample (286.0 eV), implying that the graphene is participating more deeply in the storage of K-ions. Meanwhile, at a discharging voltage of 0.01 V, the σ*-peak of the N-rich NCNF-800 sample (291.4 eV) is lower than that of the NCNF-1000 sample (292.6 eV), implying an easy diffusion of the tangled adatoms enabling the deep intercalation reaction.

As measured in the Raman spectra of NCNF-800 (Fig. S12a), the I_D/I_G ratio decreased from 0.97 to 0.94 when the sample is discharged from 1 to 0.01 V, showing an increased degree of graphitization. This phenomenon may be attributed to the absorption of K+ into nitrogen-induced defects during the potassiation process, thus reducing the disordered degree of NCNF-800.44 However, the I_D/I_G values of NCNF-1000 increased from 0.94 to 1.06 when discharged from 1 V to 0.01V (Fig.S12b). This is due to the intercalation of K+ into graphitic layers during potassiation and thus the decrease of the graphitization degree.45 Therefore, combined with in-situ TEM and ex-situ EELS, the above Raman results demonstrate that N-doping in carbon materials plays an important role on their potassium storage mechanism.

Theoretical calculations on potassium storage

To further reveal the active/storage sites in the NCNF for PIB, a series of DFT simulations were carried out (Fig. 6).37-39 The structure of the NCNF samples has been modeled, consisting of small N-doped graphene layers with atomic vacancies. The doped N are modelled as three different kinds of species: pyridinic, pyrrolic and graphitic N. While the pyridinic and pyrrolic N are located on the edges of the graphene layers and lower the diffusion energy of the K-ions, which form bonds with pyridinic N and pyrrolic N and be absorbed as K-N- ion adsorption energy exceeds 0 eV. The calculated results show that the pyridinic N-Gr, pyrrolic N-Gr and pyridinic N-Gr can store 12, 12, and 14 K-ions, respectively, in the nearby vacancies (Fig. 6a-c and Fig. S13, Supporting Information). Because of the nature of pyridinic N and pyrrolic N, they can form bonds directly with the inserted K-ions, giving more atomic vacancies around them (compared to the graphitic N). Furthermore, electron density difference maps have been calculated to investigate the effect of different N species on their bonding structure with the adsorbed K atoms (Fig. 6d-f). When one K atom is introduced into a structure with pyridinic N and pyrrolic N, the charge density of the adsorbed K atom is mainly concentrated around the pyridinic N and pyrrolic N sites. However, for the graphitic N model, the introduced K atom preferentially interacts with several nearby carbon atoms rather than with a single graphitic N. Therefore, pyridinic N and pyrrolic N display a stronger K adsorption ability than graphitic N.41 This explains the extra capacity of the N-doped samples in the high voltage range, mainly through chemical adsorption by forming a direct bond between the N and K-ions. Such an effect happens mainly on surfaces and interfaces.

Graphitic N is a little bit more negative than its surrounding C and will therefore cause intercalation of the K-ion by sharing bonds with its surrounding C. Such a process will enlarge the spacing of the local graphitic layers and lower the diffusion energy of the K-ions, which will promote a quick and full intercalation during discharge. This explains why the N-doped sample has also a large capacity in the low-energy window when the intercalation reaction dominates.

Discussion on the origin of extra capacity

The extra capacity of the N-doped nanofibers has two origins: 1) chemical absorption due to the pyridinic N and pyrrolic N induced atomic vacancies/surfaces. 2) extra intercalation capacity because of the graphitic N. In the sample with high N content, K tends to directly form bonds with pyridinic N and pyrrolic N and be absorbed as K-N-C clusters when discharged at high potential. At low potential when the intercalation reaction becomes the major K storage mechanism, the graphitic N serves as the preferential site for K-intercalation to prompt a full and deep K-intercalation. Thus there is also the extra
capacity created when charged at the low potential. Practically, the improved potassium storage properties of the N-doped NCNF-800 are also attributed to the microporous structure. The porous architecture generates a high BET specific surface area, which can provide more reaction active/storage sites and so enhance the electrode/electrolyte contact area. Additionally, interior interconnected voids and/or abundant micropores can efficiently facilitate mass transport, and hence guarantee a continuous electron transport and accommodate volume variations and strain during the potassiation/depotassiation process. As doped N will normally introduce defects into carbon matrix, the morphology of the surface and size of pores will be influenced by the N-content. Meanwhile, the doped N enhances the K\textsuperscript{+} ion surface absorption and increases the capacity, making it difficult to clearly separate the capacity contribution from surface and N-species in the two samples. However, the N-content has the major effect on the surface/pores morphology, and the mechanism of K-ions storage, thus also the increased capacity.

Figure 6. Effects of N species studied by DFT calculations. (a-c) Calculated models for K storage based on pyridinic N-Gr, pyrrolic N-Gr and graphitic N-Gr sheets with a hole containing four N atoms. (d-f) Variation of the average adsorption energy along with K atom numbers for different N-doped graphene. Brown, gray, and purple balls represent C, N, and K atoms, respectively. Yellow and blue areas represent the increased and decreased electron density, respectively.

Conclusions

The origin of the extra capacity of PIBs in the N-doped nanofibers anode has been revealed. Besides the capacity related to the chemical absorption in the high potential window (\textgreater{} 1 V), an extra capacity is created by the enhanced intercalation process in the low potential window (0.01-1 V). The chemical absorption is mainly caused by the pyridinic N and pyrrolic N in the defective sites, while the intercalation reaction is enhanced by the graphitic N which attracts K-ions and lowers the ion diffusion energy. In addition, the resultant NCNF samples possess a high surface area, tunable nitrogen species and abundant interconnected nanopores, which are favorable for potassium storage. NCNF-800 samples as a PIB anode deliver a higher reversible capacity of 290 mAh g\textsuperscript{-1} at 100 mA g\textsuperscript{-1} than NCNF-1000 samples (180 mAh g\textsuperscript{-1}). The present work provides a reasonable direction for a rational design and deep understanding of functional nitrogen-doped carbon materials toward energy-related applications.

Conflicts of interest

There are no conflicts to declare.

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References

The origin of the extra capacity of freestanding and porous N-doped carbon nanofibers was clearly revealed by systematic experimental analysis and theoretical calculations.