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Site-Selective Doping Strategy of Carbon Anodes with Remarkable K-Ion Storage Capacity

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Abstract: The limited potassium-ion intercalation capacity of graphite hampers the development of potassium-ion batteries (PIB). Edge-nitrogen doping (pyrrolic and pyridinic) has been demonstrated as an effective approach to enhance K-ion storage in carbonaceous materials. One primary shortcoming of current methods is the lack of precise control over producing edge-nitrogen configuration. In this work, we present a molecular-scale copolymer pyrolysis strategy for precisely controlling edge-nitrogen doping in carbonaceous materials. Our optimized process results in defect-rich, edge-nitrogen doped carbons (ENDC) with a high nitrogen doping level up to 10.5 at. % and high edge-nitrogen ratio of 87.6%. The optimized ENDC exhibits a high reversible capacity of 423 mAh g⁻¹, a high initial Coulombic efficiency of 65%, superior rate capability, and long cycle life (93.8% retention after three months). This edge-nitrogen control strategy can be extended to design other edge-heteroatom rich carbons through pyrolysis of copolymers for efficient storage of various mobile ions.

Introduction

Lithium-ion batteries (LIB) have been playing an increasingly significant role in hand-held electronics, electric vehicles, and electrical energy storage since 1991.^[1–3] Considering the limited lithium supplies present in the earth crust (20 ppm), and the growing need for large-scale renewable energy storage,^[4] there is a desideration to develop alternative rechargeable battery chemistries based on more earth-abundant elements, such as sodium (earth abundance 23,000 ppm),^[5] and potassium (earth abundance 17,000 ppm).^[4,6] The past decade has witnessed the rapid development in sodium-ion battery (SIB) research,^[7–10] while potassium-ion battery (PIB) remains much less explored.^[11] One of the main reasons for this reality is the lack of suitable high-performance PIB anode.^[12] Despite the success achieved in potassium metal anode,^[13–15] the long-term cycling of potassium metal anode is still a challenge. On the other hand, various alloying and intercalating anodes have attracted widespread attention.^[16–18] Graphite is the standard Li-intercalating anode, which can be fully lithiated to a stage I LiC₆ graphite intercalation compound giving a capacity of 372 mAh g⁻¹. However, when used as the anode of SIB, in carbonate electrolyte, graphite can be only

sodiated into a stage VIII NaC₆₄ compound.^[19] The failure of graphite to achieve high capacity anode in SIB has triggered the interest in intercalating K⁺ ions in graphite. Fortunately, it turns out that graphite can form a fully-potassiated stage I KC₈ compound, corresponding to a theoretical capacity of 278 mAh g⁻¹.^[20–22] Nonetheless, the rate capability and cycling stability of graphite anode for PIB are still limited due to the large volume variation (58%) during (de)potassiation, the low diffusion coefficient of K-ion, and the irreversible trapping of K atoms in graphite lattices.^[23–26] To compete with the LIB technology or achieve a low energy storage cost, the capacity of carbonaceous anodes of PIB should be improved to be comparable to the specific capacity of LiC₆. For the sake of enhanced capacity of carbonaceous anodes in PIB, several parameters must be carefully controlled, including (1) the (002) lattice spacing should be made large enough for efficient (de)potassiation;^[27,28] (2) the defect-induced adsorption mechanism should be engineered to enhance K-ion storage beyond the intercalation mechanism (here, defects refer to C-C sp³ defects, and heteroatom-doping-induced defects).^[23,24,29] Nitrogen-doping has been demonstrated as an efficient way to enhance the potassium storage capacities of carbonaceous materials owing to the increased electron negativity of defective sites for efficient adsorption of K-ions.^[23,30] In addition, edge-nitrogen (pyrrolic, and pyridinic) doping, as demonstrated by calculation and experimental study, has higher adsorption energy than sp² hybridized graphitic nitrogen doping.^[31,32] However, the state-of-art pyrolysis methods for preparing nitrogen-doped carbons from nitrogen-abundant organics are mostly done by trial and error approaches.^[31,33–35] In these approaches, the nitrogen doping of carbonaceous products cannot be precisely tuned into edge-nitrogen configurations. For instance, low-temperature pyrolysis (around 650 °C) of polypyrrole, which is typical precursor of nitrogen-doped carbons,^[32] leads to high nitrogen doping level (13.8%), but low edge-nitrogen doping ratio (55%).^[32] Thus, methods precisely synthesizing carbonaceous materials with both high nitrogen doping level, and high doping ratio of edge-nitrogen are in urgent need to enhance K-ion storage capability of carbonaceous PIB anodes.

In this work, we propose a new strategy for designing edge-nitrogen doped carbons (ENDCs) as anodes for PIB. The ENDCs are prepared from the pyrolysis of polyaniline-co-polypyrrole (PACP) precursor. During the pyrolysis process of PACP, the monomers of pyrrole and aniline show different thermal stabilities, which leads to the ordinal release of radicals generated from pyrrole, and aniline. By optimizing the pyrolysis conditions, we achieved ENDC showing both high nitrogen-doping level (10.5 at %), and high edge-nitrogen doping ratio (87.6%). This ENDC shows a high reversible capacity of 423 mAh g⁻¹, high rate capability, and superior cycling stability towards potassium storage. We show that our work constitutes a general strategy for controlling edge-nitrogen doping, and boosting the K-ion storage capability of carbonaceous anodes. This general strategy can be used in designing other edge-heteroatom-doped carbons through pyrolysis of copolymers for efficient storage of lithium, sodium and so on.

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Results and Discussion

Polyaniline-co-polypyrrole (PACP) copolymer is generally used as a precursor to prepare porous carbons for supercapacitors, and sulfur-host in lithium-sulfur batteries.^[36,37] However, these applications do rely on the porous architecture of the resultant carbons from PACP. In this work, we found the

unique advantage of PACP as a precursor to prepare nitrogen-doped carbons as PIB anodes by tuning nitrogen-doping configuration, and crystalline structure. PACP was prepared from aqueous polymerization of pyrrole and aniline monomers. Afterward, PACP was pyrolyzed in an argon atmosphere to obtain edge-nitrogen-doped carbons as anodes of PIB (carbon material obtained at a pyrolysis temperature of X °C is denoted as ENDCX) (see the synthesis route in Figure S1, Supporting Information).

Figure 1. Electron microscopy characterization of ENDCs. (a, b) SEM, and (c) TEM images of ENDC500. HRTEM images of (d, g) ENDC500, (e, h) ENDC700, and (f, i) ENDC900. (j) SEM image and EDS elemental mapping of (k) C, (l) N, (m) O, and (n) mixing of elements for ENDC500. The green arrows show some defect sites existing in ENDC500 and ENDC700, and the dash lines show some curved and long GNDs existing in ENDC900.

The PACP itself exhibits hollow sphere morphology as shown by scanning electron microscopy (SEM), and transmission electron microscopy (TEM) images (Figure S2). After pyrolysis at 500 °C, the PACP was transformed into ENDC500 with uniform sphere morphology (Figures 1a and b). The ENDC500 anode displays a hollow structure (Figure 1c). With increasing pyrolysis temperature, the hollow structures of ENDCs gradually disappear (Figure S3) due to the shrinkage effect during carbonization. Although ENDCs show analogical external morphologies (Figure S4), the intrinsic crystalline

structure does change with increasing pyrolysis temperature. High-resolution TEM (HRTEM) image of ENDC500 shows some pentagons and hexagons (distances between atoms are from 0.45 nm to 0.49 nm (Figure 1d)) which are inherited from the aniline and pyrrole monomers in PACP. With increasing pyrolysis temperature to 700 °C, ENDC700 shows some lattices with interlayer distances of 0.38 and 0.45 nm (Figure 1e). These lattices are graphenic nanodomains (GND) formed by heat-treatment. There are some defective sites between the carbon atoms which originate from the breakage of the C-C or C-N chemical bonds in pyrrole and aniline monomers. The GNDs of

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ENDCs further develop to be randomly connected and oriented (most interlayer spacings are 0.38 nm) with increasing pyrolysis temperature to 900 °C (Figure 1f) (carbon sample pyrolyzed at 900 °C shows low edge-nitrogen doping ratio, so it is denoted as NDC900). The lower-resolution HRTEMs show us the details of some defects, especially at the edge of ENDC. The ENDC500 anode shows a defective margin (Figure 1g). The ENDC700 sample also shows some defect sites, while its GNDs are more aligned than ENDC500 (Figure 1h). The NDC900 has well-developed curved turbostratic GNDs (Figure 1i) which may slow

down the potassiation process. Further, NDC900 shows some closed GNDs which may not be accessible to the K^+ cations. As predicted from HRTEM images of ENDCs, ENDC500, and ENDC700 are favorable for the efficient adsorbing and releasing of potassium ions due to the large lattice spacing, and abundant defects. The NDC900 may show slow (de)potassiation kinetics due to the smaller interlayer spacing, and curved GNDs. Energy-dispersive X-ray spectroscopy (EDS) mapping shows uniform elemental distributions of C, N, and O, which demonstrates that ENDC500 is doped with heteroatoms of nitrogen and oxygen.

Figure 2. Physical characterization of ENDCs. (a) XRD patterns of ENDCs and NDC900. (b) TGA curves of ENDCs and NDC900 tested in air. (c) Raman spectra of ENDCs and NDC900. (d) MS spectra of PACP. (e) EPR spectra of ENDCs and NDC900. (f) N 1s high-resolution XPS spectra of ENDC500, inset schematic shows the atomic-scale structure of ENDC500.

After the pyrolysis of PACP at 400 °C for 2 hours, most PACP structure remains in NDC400 (Figure S5). With higher pyrolysis temperatures, ENDC500, ENDC700, and NDC900 exhibit amorphous carbon structure indicated by the (002) hump peaks in X-ray diffraction (XRD) patterns (Figure 2a). The (002) hump peaks of ENDCs reveal the amorphous nature of ENDCs without well-defined (002) interlayer spacing. Since XRD patterns can not clarify the arrangements and lengths of turbostratic GNDs in amorphous carbons,^[38] *R* value, introduced by Dahn *et al.*, was applied to evaluate the order degree of amorphous carbons.^[39] With the increase of pyrolysis temperature, ENDCs show increased *R* values from 1.66 of ENDC500 to 1.85 of ENDC700 and finally to 1.91 of NDC900, which indicates the increased order degree and is in good agreement with the TEM results. With increasing pyrolysis temperature, the thermostabilities of ENDCs increase (decomposition temperatures are 517, 566, and 591 °C for ENDC500, ENDC700, and NDC900, respectively, as shown by thermogravimetric analysis (TGA) in Figure 2b), which demonstrates the enhanced structural order and reduced defect densities in ENDCs. The ENDC500 shows a much lower I_D/I_G ratio (0.77) compared with ENDC700 (0.88) and NDC900 (0.90) (Figure 2c), which is ascribed to the fact that ENDC500 inherits some hybridized sp^2 pentagon and hexagon structures from PACP. Similar results can be found in ENDC400 (Figure S6),

and the low-temperature pyrolyzed polyaniline from other researches.^[40] The high I_D/I_G ratios of 0.88 of ENDC700, and 0.90 of NDC900 indicates that the pristine PACP is decomposed, and then transformed into amorphous carbon.^[41] To further track the structural evolution of PACP during pyrolysis, TGA, differential scanning calorimetry (Figure S7a) coupled with mass spectroscopy (MS) (Figure 2d) was used to identify the chemical species released during pyrolysis. During the pyrolysis of PACP, small molecules, such as CO_2 , NH_3 , H_2O , and H_2 , are detected through the whole pyrolysis process. Some big prototypical radicals like C_4NH_3 (atomic unit mass, 65), and C_6H_5 (atomic unit mass, 77) are released from the decomposition of pyrrole and aniline (Figure 2d, and S7b), respectively. However, C_4NH_3 starts to release at ca. 180 °C, while C_6H_5 starts to release at a higher temperature of ca. 230 °C, which indicates that aniline is more stable than pyrrole in the PACP precursor. At temperatures above 500 °C, the release rate of C_4NH_3 decreases. Thus, the structure of pyrrole with its nitrogen has been incorporated into the carbon skeleton. However, at the pyrolysis temperature of 500 °C, C_6H_5 radical has a high releasing rate. The remaining aniline monomers decompose, and thus are incorporated into the carbon skeleton resulting in nitrogen doping in carbon skeleton. The release of C_6H_5 creates carbon vacancies for dangling bonds, which facilitates the formation of edge-nitrogen doping (pyridinic, and pyrrolic). C_6H_5 radicals continue to release until a temperature of 700 °C, which facilitates the formation of

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edge-nitrogen doping within the temperature range $< 700\text{ }^{\circ}\text{C}$. At temperatures ranging from 500 to $700\text{ }^{\circ}\text{C}$, there are carbon vacancies caused by the continued releasing of C_6H_5 , which is in good agreement with the TEM results. At temperatures above $700\text{ }^{\circ}\text{C}$, the main reactions are the release of small molecules such as CO_2 , H_2 , and H_2O . The release of these small molecules could create micropores.^[42] The decomposition modality mentioned above causes the evolution of different pore structure in ENDCs (Table S1). The ENDC500 shows larger average pore size (3.5 nm) and lower specific surface area ($269.8\text{ m}^2\text{ g}^{-1}$) due to the release of large radicals (C_4NH_3 and C_6H_5) at $500\text{ }^{\circ}\text{C}$. The NDC900 shows high specific surface area ($376.6\text{ m}^2\text{ g}^{-1}$), and small average pore size (2.9 nm) due to the release of small molecules (H_2 , CO_2 , and H_2O) at $900\text{ }^{\circ}\text{C}$ (Figure S8). Electron Paramagnetic Resonance (EPR) (Figure 2e) was further used to interpret the structures of ENDCs. In Figure 2e, Lorentzian lines centering at $g=2.0027$ is observed for ENDCs, indicating the generation of unpaired electrons on π -conjugated carbon atoms. The ENDC500 shows much lower linewidth (8.25 G) than the ENDC700 (63.05 G), and NDC900 (144.70 G), which demonstrates that the unpaired electrons are localized in ENDC500, which is in agreement with the partial decomposition of the pristine sp^2 hybridized structure in PACP. However, the unpaired electrons of ENDC700, and NDC900 are more delocalized due to the enlarged GND in the carbon skeleton. The

partially decomposed structure of ENDC500 was confirmed by Fourier-transform infrared spectroscopy (FTIR) (Figure S9). Due to the existence of pristine pentagon and hexagon geometries derived from PACP, the ENDC500 shows higher sp^2/sp^3 ratio (1.14) compared with ENDC700 (0.65), and NDC900 (0.53) (Figure S10, and Table S3). As the defective structure of ENDC500 and ENDC700 is due to the release of C_6H_5 radicals, ENDC500 and ENDC700 show higher edge-nitrogen doping level as evidenced by the $\text{N } 1\text{s}$ spectra (Figure 2f and Figure S11a). The NDC900 shows high graphitic nitrogen ratio (Figure S11b) as most nitrogen dopants are incorporated into the in-plane GND. On the other hand, the ENDC500 shows a high concentration of nitrogen ($10.5\text{ at. } \%$), and high edge-nitrogen ratio (87.6% with respect to all the nitrogen species) (Table S2). The ENDC700 has a nitrogen concentration of $8.0\text{ at. } \%$, and an edge-nitrogen ratio of 78.3% which is still higher than NDC900 ($3.4\text{ at. } \%$ and 50.3% respectively) (Figure S11c, and Table S4). The ENDC500 and ENDC700 sample show highly defective structure, and high edge-nitrogen ratio, which is in good agreement with the TEM, Raman, EPR, and TGA-MS analysis. The ENDC500 achieves both high nitrogen doping level, and high edge-nitrogen doping ratio, which is beneficial for the interfacial adsorption storage of K-ions. The opened lattice structures of ENDC700, and ENDC500 are expected to be beneficial for high rate K-ion diffusion.

Figure 3. Schematic diagram showing the influence of pyrolysis temperature on the atomic-scale structures of ENDCs and NDC900. Higher edge nitrogen doping can be realized at low pyrolysis temperature. Further, enhanced K-ion diffusion kinetics can be expected at highly-defective, edge-nitrogen dominated structures of ENDC500 and ENDC700. NGC900 shows long-diffusion pathways and less edge-nitrogen doped carbon lattice. Legend: carbon atom (black), hydrogen atom (silver grey), nitrogen atom (blue), potassium atom (purple).

As discussed above, the ordinal decomposition of radicals from pyrrole (C_4NH_3), and aniline (C_6H_5) in PACP results in both high nitrogen doping, and high edge-nitrogen doping ratio for the ENDC500 sample (Figure 3). The opened edge defects are beneficial for efficient K-ion diffusion, while the edge-nitrogen

doping contributes capacity by acting as active sites for efficient adsorbing potassium ions. For the NDC900 sample, higher pyrolysis temperature causes significant decomposition of PACP, in which turbostratic GNDs develop while the overall nitrogen-doping level decreases. Most importantly, the edge-nitrogen doping level of NDC900 decreases (Figure 3). The curved

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turbostratic GNDs in the NDC900 sample could limit potassiation, while the long curved graphene layers could limit diffusion, which

is expected to degrade the K-ion storage performance of the NDC900 sample.

Figure 4. Electrochemical performances of ENDC500, ENDC700, and NDC900. (a) CV curves of ENDC500 at a scan rate of 0.1 mV s⁻¹. (b) GCD curves of ENDC500 at a GCD current of 50 mA g⁻¹. (c) Capacities and ICEs compared between high-capacity carbonaceous materials reported in literatures, and ENDC500, descriptions of the literature samples are in the main text and in Table S5. (d) Rate performances of ENDCs, and NDC900. (e) Long-term cycling stabilities of ENDCs, and NDC900 at a GCD current of 200 mA g⁻¹. (f) *b* values of ENDCs and NDC900. Capacitive contributions of (g) ENDC500, (h) ENDC700 and (i) NDC900.

Figure 4a shows the cyclic voltammetry (CV) curves of ENDC500 electrode, where the cathodic peak around 0.8 V in the first cycle corresponds to the formation of solid electrolyte interphase. After the first cycle, the CV curves overlap well, indicating the highly reversible characteristic of the ENDC500 electrode. The cathodic peak close to 0 V corresponds to the intercalation of K-ions, while the hump anodic peak around 0.75 V corresponds to the deintercalation of K-ions. In the initial cycles, the anodic peak at 0.7 V shifts slightly and stabilizes due to the structural re-arrangement during (de)potassiation.^[23] Compared with ENDC500, ENDC700 and NDC900 electrodes show smaller areas of the CV curves (Figure S12), indicating decreased reversible capacity. The galvanostatic charge-discharge (GCD) curves (Figure 4b) demonstrate similar behavior as the CV curves. Specifically, the ENDC500 electrode displays a first cycle discharge capacity of 828 mAh g⁻¹ with a first cycle charge capacity as high as 481 mAh g⁻¹, corresponding to an initial Coulombic efficiency (IEC) of 65%. The reversible capacity and IEC of ENDC500 electrode reported in our work is significantly higher than previously reported carbonaceous anodes, as shown

in Figure 4c, and Table S5, such as pyridinic N-doped porous carbon monolith (PNCM, 388 mAh g⁻¹, IEC <20%),^[43] nitrogen/oxygen dual-doped hierarchical porous hard carbon (NOHPHC, 365 mAh g⁻¹, 25%),^[44] S and N co-doped thin carbon (S/N@C, 320 mAh g⁻¹, 23%),^[45] nitrogen-doped carbon nanosheets (N-CNS, 300 mAh g⁻¹, 20%),^[46] nitrogen-doped carbon nanofibers (NCNF, 248 mAh g⁻¹, 49%),^[32] and nitrogen-doped necklace hollow carbon (NHC₂-NH₃/Ar, 277.8 mAh g⁻¹, <30%).^[31] The much higher capacity of the ENDC500 electrode than graphite, and high ICE compared with most reported carbon anodes endow it a promising anode for PIB. Most importantly, the capacity of ENDC500 anode mainly occurs at 0.1–2 V, which could enhance the energy density of a full PIB cell, while avoiding the risk of potassium dendrites deposition. Since there are some remaining PACP structures in NDC400 electrode, it only shows a reversible capacity around 350 mAh g⁻¹, as shown in the GCD curve in Figure S13 (note that pristine PACP shows near-zero capacity). The rate capabilities of ENDC electrodes were tested at different GCD current densities from 50 to 5000 mA g⁻¹ as shown in Figure 4d (corresponding GCD curves are shown in Figure S14). After 10 GCD cycles, at a current density of 50 mA

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g^{-1} , the ENDC500 electrode shows a reversible charge capacity of 423 mAh g^{-1} , while the charge capacities of ENDC700, and NDC900 electrodes are 327 mAh g^{-1} , and 166 mAh g^{-1} , respectively. Both ENDC500, and ENDC700 electrodes show higher rate capabilities compared with NDC900 (Figure 4d). The ENDC500 electrode shows high capacities of 423, 336, 290, 238, 195, 148, and 74 mAh g^{-1} at current densities of 50, 100, 200, 500, 1000, 2000, and 5000 mA g^{-1} , respectively. The corresponding capacities for the ENDC700 electrode are 330, 281, 251, 192, 130, 76, and 26 mAh g^{-1} , while for NDC900 they are 168, 113, 71, 35, 16, 3, and 0.6 mAh g^{-1} . The above results demonstrate that ENDC500 electrode not only has high capacity, but also has high rate capability, which is ascribed to the high edge-nitrogen doping level and highly defective structure. ENDC700 electrode also shows decent rate capability owing to its defective surface, and moderate nitrogen doping. The long-term cycling stabilities of ENDC electrodes were tested at a GCD current density of 200 mA g^{-1} (Figure 4e). The ENDC500 anode shows high stability during 660 GCD cycles (capacity retention of 93.8% with a remaining capacity of 305 mAh g^{-1} , test lasted for 3 months) which is much higher than most recently reported carbon anodes.^[27,47] In comparison, the ENDC700 electrode shows a capacity retention of 73% with a remaining capacity of 193 mAh g^{-1} after 300 cycles. The NDC900 electrode shows the lowest remaining capacity of only 62 mAh g^{-1} after 420 cycles. As discussed, the ENDC500 electrode shows high edge-nitrogen doping, and high surface defect concentration, both of which are beneficial for high capacity and high rate capability. While the closed GNDs of NDC900 electrode are inaccessible to K-ions. The unique edge-defect-rich structure of ENDC500, and ENDC700 is beneficial for K-ions diffusion, as indicated by the low b values (Figure S15, and experimental details in Supporting Information) of ENDC500, and ENDC700 electrodes (Figure 4f). A b value of 0.5 suggests that the electrochemical reaction is diffusion-limited, while a b value of 1.0 suggests a surface-dominated electric-double layer or Faradaic processes.^[23,46] The b value of NDC900 electrode is very close to 0.5, indicating diffusion-limited intercalation kinetics, which is caused by the developed graphene layers inside the carbon matrix of NDC900. While, the b values of ENDC500, and ENDC700 are higher than 0.5, which suggests that the storage of K-ions in ENDCs result

from combined adsorption/intercalation mechanism. The capacitive contribution was calculated based on Dunn's method (see experimental details in Supporting Information) at a low scan rate of 0.2 mV s^{-1} . The ENDC500 electrode shows a capacitive contribution of 64.5%, while the ENDC700 electrode shows a capacitive contribution of 61.1%. The low capacitive contribution of NDC900 (40.2%) can be attributed to its developed GNDs. The ENDCs electrodes show low capacitive contributions at potentials below 1 V, which is an indication that the energy storage mechanism of NDC900 in this region is dominated by K-ion intercalation.^[23] As calculated by density functional theory (DFT), oxygen functional groups adsorb K-ions at ca. 1.7 V.^[35] However, the much lower capacity contribution of NDC900 at 1.7 V (Figure 4i) compared with that of ENDC500 (Figure 4g) demonstrates that the oxygen functional groups contribute much less reversible capacity compared with nitrogen functional groups.^[23]

TEM-EDS mapping demonstrates that there is no phase separation between K and carbon (Figure S16), which proves the combined intercalation/adsorption mechanism of K-ion storage in ENDCs. *Ex-situ* Raman and HRTEM were further used to detect the crystalline structure of ENDC500 at different GCD states (Figure S17). The I_D/I_G ratio for the pristine ENDC500 anode was determined to be 0.77. When the ENDC500 anode was fully potassiated at 0.01 V, its I_D/I_G ratio became 0.73, and when it was depotassiated to 3.0 V, its I_D/I_G ratio recovered to 0.79. The decreased I_D/I_G ratio of the potassiated ENDC500 indicates the ordering of carbon lattice after potassiation.^[48] HRTEM was also used to detect the crystalline structure evolution of ENDC500 electrode during (de)potassiation. Pristine ENDC500 shows amorphous structure (Figure S17b). Fully-potassiated ENDC 500 anode shows a somewhat aligned carbon lattice (Figure S17c), which could be due to electrostatic forces between adsorbed K-ions and carbon. The structure of ENDC anodes recovered after depotassiation (Figure S17d), which demonstrates their superior structural stability during (de)potassiation. After 660 GCD cycles, the ENDC500 electrode shows undamaged sphere morphologies and 3D framework (Figure S18), which demonstrates the robust structural stability of ENDC 500 electrode during (de)potassiation.

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Figure 5. Theoretical calculations of K-adsorption in different N-doped configurations. Top view of a single K atom adsorbed in the (a) N6, (b) 2N6, (c) 3N6, (d) 2N5, (e) 3N5 configurations. (f) Adsorption energy as a function of N doping configuration. Legend: black represents carbon atom, silver grey represents hydrogen atom, blue represents nitrogen atom, and purple represents potassium atom.

To further understand the superior K-ion storage capability of edge-nitrogen rich ENDC500 electrode, the relative adsorption energies of K atoms adsorbed on carbon lattice with different nitrogen-configurations were calculated using DFT. The relative binding energy (E_b) for a K atom adsorbed on a graphitic nitrogen (NQ) structure is -0.26 eV (Figure S19a). The E_b greatly increase as nitrogen dopant become edge-nitrogen configurations (pyrrolic (N5), and pyridinic (N6)) (Figure S19b, and Figure 5a). The E_b for N5 configuration is -1.92 eV, and the E_b of N6 configuration is -2.07 eV (Figure 5f). The increased number of edge-nitrogen atoms at a defective site (Figure 5b, c, d and e) significantly enhances the adsorption energy (Figure 5f), however, the average E_b decreases. The adsorption energy of three pyrrolic-nitrogen configuration (3N5) is -2.94 eV, while the adsorption energy of three pyridinic-nitrogen configuration (3N6) is -2.86 eV. Thus, the defective structure in ENDC500 enhances the distribution of edge-nitrogen atoms, leading to more N5, and N6 type configurations, which enhances the capacity of adsorbing potassium. The above results show that for carbonaceous materials, it is important to increase the edge-nitrogen doping level while keeping the defective structures to increase the K-ion adsorption energy of carbonaceous materials.

Conclusion

We have developed a strategy for designing edge-nitrogen doped carbons (ENDC) for efficient K-ion storage. Our approach uses a copolymer pyrolysis process, in which two starting monomers (aniline and pyrrole) have different thermal stabilities. During pyrolysis of the polyaniline-co-polypyrrole (PACP) copolymer, the undecomposed pyrroles are incorporated into the carbon skeleton, while the later released radicals from aniline create abundant defective sites, which induces most doped nitrogen atoms to adopt edge-nitrogen configurations. The high edge-nitrogen doping coupled with the defect-rich structure of ENDC provides high reversible capacity, excellent rate capability, and superior cycling stability. The optimized ENDC shows a stabilized reversible K-ion storage capacity of 423 mAh g⁻¹ which is comparable to state of art the Li-ion storage capacity of graphite anode. Our strategy can be generally applied for the synthesis of other edge-heteroatom-doped carbonaceous anodes for enhanced storage of lithium, sodium and so on.

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Keywords: Potassium-ion battery; Carbon; Edge-nitrogen doping; Anode; Adsorption energy.

Conflict of interest

The authors declare no conflict of interest.

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Controllable Edge-Nitrogen Doped Carbon for Potassium Ion Battery

W. Zhang, Z. Cao, W. Wang, E. Alhajji, A. H. Emwas, P. M. F. J. Costa, L. Cavallo, H. N. Alshareef*

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Site-Selective Doping Strategy of Carbon Anodes with Remarkable K-Ion Storage Capacity