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Nitrogen Configuration Dependent Holey Active Sites Toward Enhanced K⁺ Storage in Graphite Foam

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Abstract

The nitrogen doping generally plays an important role in alkali-ion storage. Herein the nitrogen doping effect on K^+ storage in graphite foam is explored. Experimental and theoretical calculations reveal that the K^+ storage behavior is strongly dependent on nitrogen doping concentration and doping configurations. Specifically, high doping level i) provides more pyridinic/pyrrolic nitrogen content, thus creating more holey structures for K^+ storage, ii) enlarges interlayer spacing to facilitate K^+ intercalation, and iii) increases electronic conductivity to ensure fast kinetics. For the first time, we proved that the holey structure, rather than nitrogen doping, contributes to the capacity enhancement for carbon-based potassium ion batteries. Our investigations promote better understanding of K^+ ion storage mechanism in doped graphite and provide invaluable guidance to optimize carbon-based electrode design for high-performance potassium ion batteries.

1. Introduction

Potassium ion batteries (KIBs) show great potential in terms of geologically abundant K element (1.5 wt. %) [1], lower redox potential of K^+/K (-2.94 V vs. standard hydrogen redox potential) compared to Na^+/Na (-2.71 V) [2-4], higher mobility due to weaker Lewis acidity of K^+ compared with other alkalis [4], and reversible intercalation of K^+ in graphite, with a theoretical capacity of 279 mAh g⁻¹ via the formation of first stage graphite intercalation compounds (K-GICs), KC_8 [4, 5]. However, the much larger radius of K^+ (1.38 Å) compared to Li^+ (0.76 Å) makes it difficult for K^+ intercalation [6]. Moreover, the intercalation/de-intercalation of K^+ could cause large volume change (61% for graphite) and structural distortion/collapse. This will induce the loss of active sites and lead to poor reversibility/stability upon long-term cycling [7]. To overcome these limitations of carbon based KIBs (i.e. low capacity, inferior cycling stability and poor Coulombic efficiency), the structural and morphological modifications of electrode materials, including the tuning of interlayer spacing [8], specific surface area [6] and creation of new active sites for K^+ storage [9], are highly desired.

So far, a variety of carbonaceous based anode materials have been investigated for KIBs since 2010s. Roughly, they can be divided into modified graphite [10, 11], biomass derived carbon materials [12-14], versatile designed carbon nanostructures [8, 15-17] and heteroatom (N, O, S, F) doped carbon materials [18-22]. The well-designed, modified or doped carbon materials usually have increased surface area, enriched active sites for K^+ storage and enhanced electronic conductivity, resulting in high specific capacity and good rate capability for KIBs. The modified graphite, like expanded graphite [11] and activated carbon [23], exhibits enlarged interlayer distance in (002) crystal planes, contributing to high reversibility and long cycling life. Besides modified

graphite, the short-range ordered mesoporous carbon with large interlayer spacing and unique structure has been also proved to be beneficial for high rate capability and good cycling stability. The volume expansion was reduced to 7% via K^+ intercalation, indicating the effective enhancement of electrochemical performance by enlarging the interlayer space [8]. Large surface area of carbon-based electrode materials, like hierarchical porous hard carbon [21], is favorable for high specific capacity due to the massive surface defects introduced for K^+ storage.

The heteroatom doping is another promising strategy to improve K^+ storage. Specifically, nitrogen-doping is of particular interest benefiting from the following merits: i) the doped N could enlarge the interlayer space of carbon materials, thus facilitating the intercalation/de-intercalation of K ions [19]. ii) The introduction of structural defects and disorders upon N-doping may alleviate the volume expansion to a certain extent, ensuring long cycling life [18-20, 24]. And iii) the conductivity could be greatly enhanced, beneficial for good rate performances [25]. The *in-situ* Raman spectra have been used to study the K^+ storage mechanism in nitrogen doped graphite. It was concluded that the nitrogen doping not only promotes the fully K^+ intercalation process, but also introduces more active sites for efficient K^+ storage, boosting the specific capacity significantly [18, 21]. Meanwhile, the doping induced enlarged interlayer spacing is also beneficial for K^+ intercalation, contributing to enhanced capacity and stability [26]. To the best of our knowledge, there is no comprehensive study on the effects of doping concentration and configurations on K^+ storage. Besides, it is generally considered that the remarkable enhancement in capacity of N-doped carbonaceous materials is owing to large amounts of K^+ adsorption on N doped sites. However, there is no solid evidence to support it.

Herein, the effect of nitrogen doping concentrations and doping configurations on K^+ storage have been studied in self-supported graphite foam. It is found that i) the percentage of pyridinic (PD) and pyrrolic (PL) nitrogen increases with the increased nitrogen content, and ii) the PD/PL introduces holey structures with more active sites for efficient K^+ storage. For instance, at a nitrogen doping level of 8.47 at. % (NGF-8.47), the PD and PL, together reaches 89 % in total doping, with a large total pore volume of $0.212 \text{ cm}^3 \text{ g}^{-1}$, which is much higher than that of NGF-1.03 and NGF-2.22 (0.085 and $0.118 \text{ cm}^3 \text{ g}^{-1}$, respectively). The increased pore volume originates from large amounts of mesopores (around 10.9 and 14.6 nm), which could accommodate more K ions and facilitate contact between electrolyte and electrode. Meanwhile, the interlayer spacing is also enlarged to 0.346 nm, favorable for reversible K^+ intercalation. The increased pore volume and interlayer distance according to large N doping intensities, together contribute to a high specific capacity (247 mAh g^{-1} at 10 mA g^{-1}) and good cycling stability (86% capacity retention after 200 cycles' test). The large amounts N doping also ensures considerable enhancement in conductivity, beneficial for superior rate performances.

2. Experimental Section

2.1 Chemicals & Reagents:

Nickel foams (NFs) (Pore size, 0.1-10 mm) were bought from Shanghai Zhongwei New Material Co., Ltd. Chemicals including melamine ($C_3H_6N_6$) (ACS reagent, $\geq 99 \%$), Iron (III) chloride ($FeCl_3$) (reagent grade, 97%) and reagents Ethylene carbonate (EC, 98%)/ Diethyl carbonate (DEC, 99%) were purchased from Sigma and used as received. The potassium bis(fluorosulfonyl)imides (KFSI) (Cica-Reagent) was bought from Kanto chemical CO., INC, Japan. The reagents hydrochloride acid (37%) and ethanol (analytic reagent grade) were purchased from VWR CHEMICALS (PROLABO)

and Fisher Chemical. The deionized water (18.2 M Ω , DIW) was used for cleaning samples.

2.2 Material synthesis:

N-doped graphite foam (NGF) was synthesized by the modified chemical vapor deposition (CVD). Nickel foams (NFs) with the areal size of $\sim 20\text{ cm}^2$ and thickness $\sim 1\text{ mm}$ were treated by 5 wt.% hydrochloric acid prior to be used as templates. Then the NF templates were placed at the center of the horizontal quartz tube. The nitrogen/carbon precursor, melamine, was placed at the low temperature zone. To grow NGFs, the NFs were heated to 1000 $^{\circ}\text{C}$ in N_2 (20 sccm) with heating rate of 10 $^{\circ}\text{C}/\text{min}$. Meanwhile, the precursor, melamine, located at low temperature zone reached pyrolysis temperature ($\sim 400\text{ }^{\circ}\text{C}$). NGF-1.03, NGF-2.22 and NGF-8.47 on NF skeletons were obtained by keeping furnace at 1000 $^{\circ}\text{C}$ for 30, 10 or 20 mins, respectively. The Nitrogen doping content can be well adjusted via controlling the annealing time. The control sample of undoped graphite foam (GF) was obtained with the CH_4 as the precursor following previous experimental method [27]. Self-supported GF and NGFs were achieved after removing of NF skeletons in 0.5 M FeCl_3 solution. The NGFs with different nitrogen concentrations are denoted as NGF-x (x represents the nitrogen doping atomic ratio) and used as electrodes without any binder or conductive additives. NGF-1.03, NGF-2.22 and NGF-8.47 are studied in this work.

2.3 Materials Characterization:

The morphologies of NGF were studied by Field Emission Scanning Electron Microscope (FE-SEM) (Model Jeol JSM 6700F) and Transmission Electron Microscope (JEOL 2010 UHR, and JEOL 2100 UHR, TEM, acceleration voltage: 200 kV). The crystallinity and the graphitization of NGF obtained at different experimental

conditions was studied by X-Ray Diffraction (XRD, Bruker D8 Advance with Cu-K α radiation of $\lambda = 0.15406$ nm) and Raman spectroscopy (Renishaw, laser wavelength: 532 nm), respectively. Electrode materials were investigated on X-ray Photoelectron Spectroscopy (XPS), using a VG ESCALAB 220i-XL system with a nonmonochromatic Al K α photon source ($h\nu = 1486.7$ eV). Calibration of the binding energy scale was set using the reference at 284.6 eV. The nitrogen adsorption and desorption tests were conducted on surface area and porosity analyzer, Tristar Model ASAP 2020.

2.4 Computational details

All the calculations were carried out on the basis of density functional theory (DFT) [28], as implemented in VASP code [29, 30]. The potentials of atoms were described by accurate frozen-core full-potential projector augmented-wave pseudopotentials (PAW) method. Generalized gradient approximation (GGA) with the parameterization of Perdew, Burke and Ernzerhof (PBE) was used for electron interaction of exchange correlation [31]. The Brillouin zone was sampled by a Γ -centered high density k -grid. A kinetic energy cutoff of 550 eV and a k -point spacing of $0.08 \text{ \AA}^{-1}$ was found to be sufficient to ensure that the total energy is converged at 1 meV/atom level. The spin-polarization effect was considered in the calculations. With the supercell method, a vacuum space of 15 $\text{\AA}$ is set to avoid artificial periodic interactions in z direction. It is noticed that the dispersion effect doesn't take an important role in the adsorption of K in the pore structures of graphene layer and thus the van der Waals interaction is ignored in the calculation.

2.5 Electrochemical test:

NGF with different concentrations of nitrogen-based batteries were assembled in a glovebox with Ar atmosphere. The NGF, the Whatman grade GF/D glass microfiber filter separator with 1.0 M $\text{KN}(\text{SO}_2\text{F})_2$ (KFSI) in EC/DEC (1:1 in volume) electrolyte and the K metal were sealed accordingly in a coin cell. The NGFs were cut into small disks (Diameter: 1 cm, Area: 0.785 cm^2 , Areal weight: 1.9 mg cm^{-2}). Every disk has a total weight of around 1.5 mg. The photographs of fresh undoped-GF, NGF-1.03, NGF-2.22 and NGF-8.47 disks are shown in Fig. S1. The specific capacity of every disk electrode is calculated based on the actual disk weight. $\text{KN}(\text{SO}_2\text{F})_2$ (KFSI) is chosen as electrolyte in this work due to its high solubility in both PC and EC [4, 32]. Moreover, FSI-based electrolytes are more favorable for a highly stable and effective solid electrolyte interface (SEI) than PF_6 -based electrolytes in lithium ion batteries.[33] Cyclic voltammetry curves from 0.01 V to 1.5 V (vs. K^+/K) and Nyquist plots in the frequency range of 100 kHz to 0.01Hz were performed on Solartron Analytical, CellTest system, 1470E. The galvanostatic charge discharge were conducted on Neware Technology testing system in the voltage range of 0.01-1.0 V versus K^+/K .

3. Results and discussions

The self-supported NGFs with different nitrogen concentrations and configurations could be easily obtained through the facile one-step chemical vapor deposition (CVD) method, including the pyrolysis of melamine and the deposition of graphite foam (GF) on nickel foam (NF) simultaneously (Fig. 1). Melamine, a white monoclinic crystal at room temperature, has a melting temperature of 354°C under barometric pressure. It is easy to sublime with frequent heat, with a sublimation temperature around 300°C [34]. In our approach, melamine is placed in the low-temperature zone, the template/catalyst, while NFs are placed in the high-temperature zone. When the temperature increases to 1000°C , the pyrolysis and sublimation of melamine happen

in the low-temperature zone, around 400 °C. The pyrolysis products, like g-C₃N₄ (according to C₃N₆H₆ (s) → g-C₃N₄ (g) + 2 NH₃(g) [35]) and the sublimated melamine (C₃N₆H₆) are catalyzed by nickel at high temperature, following by the diffusion and recombination of C and N atoms into nickel foams, resulting in *in-situ* doped nitrogen graphite foam-nickel foam (NGF-NF).

Fig. 1 The schematic illustration of nitrogen doped graphite foam-nickel foam (NGF-NF) via chemical vapor deposition.

The branch structure of doped NGFs and undoped GF is well preserved after etching of NF (Figs. S2a-S2f, Figs. S3a-S3b). In the high-magnification SEM images, rough and rugged surfaces are observed, which could be favorable for electrolyte accommodation. Energy-Dispersive X-ray Spectrometry (EDS) (Fig. S2g) mapping illustrates a uniform elemental distribution of C, N and O, indicating homogenous incorporation of nitrogen in carbon matrix. As shown in Figs. 2a-c, the high-resolution transmission electron microscopy (HRTEM) images of NGFs reveal the highly graphitic feature although the nitrogen doping concentrations and configurations are different. All NGFs consist of dozens of graphene layers with a thickness around 10 nm, which are quite promising for K ion intercalation owing to facilitated ion/electron transportation and enriched exposure active sites [18, 22]. Interestingly, NGFs exhibit expanded interlayer distance compared to graphite (0.335 nm) [36], which is probably due to the nitrogen doping effect. Specifically, the interlayer spacing is enlarged upon N doping, i.e., the interlayer spacing is 0.346 nm for NGF-8.47 (Fig. 2c), which is larger

than both NGF-1.03 (Fig. 2a, 0.340 nm) and NGF-2.22 (Fig. 2b, 0.342 nm). In addition, NGF-8.47 exhibits a curved and open lattice structure compared to NGF-1.03 and NGF-2.22, thus consisting much abundant edges. This is beneficial for K^+ capture and intercalation [20]. The sharp peak around $26.05^\circ \pm 0.1^\circ$ (Fig. 2d) is indexed to (002) plane (JCPDS 75-1621). The obvious shifting of (002) peak towards lower angle reveals that NGF-8.47 exhibits the largest interlayer spacing compared to NGF-1.03 and NGF-2.22, in agreement with the HRTEM study.

The Raman spectra of NGFs (Fig. 2e) exhibit two distinct peaks, D band (1350 cm^{-1}) and G band (1580 cm^{-1}) [37]. The intensity ratios of D band with respect to G band (I_D/I_G) are calculated to be 0.83, 1.25 and 1.41 for NGF-1.03, NGF-2.22 and NGF-8.47, respectively [38, 39]. The high intensity of D band indicates highly defective structures, arising from nitrogen doping [19, 38-41]. This is different from the defect-free nature of undoped graphite foam, in which no D band is identified (Fig. S3c). More interestingly, TEM images reveal the holey/defective structures in doped NGFs (Fig. S4). Mesopores with lateral dimension of $\sim 10\text{ nm}$ are clearly demonstrated in NGFs, especially for NGF-8.47 (Fig. S4c). For NGF-1.03 and NGF-2.22, holey structures located at interlaced lattice are also identified (Figs. S4a and S4b). The mesoporous feature originating from nitrogen doping were further examined by the nitrogen adsorption-desorption isotherms, in which a type IV isotherm is achieved (Fig. 2f) [42]. Based on Brunauer-Emmett-Teller (BET) method, the specific surface areas of NGF-1.03, NGF-2.22 and NGF-8.47 were calculated as 16.1, 22.6 and $45.6\text{ m}^2\text{ g}^{-1}$, with corresponding total pore volumes of 0.085, 0.118 and $0.212\text{ cm}^3\text{ g}^{-1}$, respectively. The pore size distribution curves (Fig. 2h) indicate that NGFs have a large portion of mesopores around 10.9 and 14.6 nm. Specifically, NGF-8.47 contains more mesopores, i.e., 10.9 nm pores, compared to NGF-1.03 and NGF-2.22. These holey/defective

structures are intrinsically induced by N-doping, especially pyridinic/pyrrolic nitrogen. The mechanism will be discussed later. These structures can promote the K^+ mobility and facilitate the K^+ ions' access to active sites during charge and discharge process [14]. Additionally, it could accommodate the structural changes via K^+ intercalation and de-intercalation and enhance the cycling stability [17].

Fig. 2 Morphological and structural characterizations of NGFs. HRTEM images of (a) NGF-1.03, (b) NGF-2.22 and (c) NGF-8.47. Inset of (a, b, c): The corresponding FFT patterns. (d) XRD patterns and (e) Raman spectra of NGF-1.03, NGF-2.22 and NGF-8.47. Inset of (f): XRD

spectra centered at the characteristic peak of (002) crystal plane. (g) Nitrogen adsorption and desorption isotherms and (h) pore size distribution of NGF-1.03, NGF-2.22 and NGF-8.47.

The nitrogen doping concentrations of NGFs are determined by XPS analysis. The N1s spectrum was fitted into three sub-peaks, assigning to PD (~398.8 eV), PL (~400.2 eV) and graphitic nitrogen (~401.9 eV) respectively (Figs. 3a-c) [43, 44]. The ratio of three bonding configurations (PD, PL and Graphitic N) in whole electrode materials (Fig. 3d) are calculated and elucidated based on the XPS results. The PD/PL nitrogen doping increases rapidly with the increasing of total nitrogen doping (from 0.72 at. % to 7.54 at. %), while graphitic nitrogen increases much slower (0.31 at. % to 0.94 at. %), indicating that large doping concentration favors for PD/PL doping as well. The PD and PL nitrogen (7.54 at. % in NGF-8.47) are believed to be more effective to improve the reversible capacity by creating large intensities of holey structures and active sites for K ion storage [9, 18]. Meanwhile, graphitic nitrogen located at the center and bonded with three sp^3 carbon atoms could effectively enhance the conductivity of the graphitic carbon matrix as the electron-donor characteristic could be changed significantly via this graphitic N doping [21]. Thereinto, NGF-8.47 with the highest graphitic N doping is expected to deliver the best electronic properties among all NGFs. The high resolution C1s spectra in Figs. S5a-S5c further demonstrate that nitrogen, as well as oxygen are doped in carbon matrix with bonding identifications around 285.3 eV (C-N), 286.2 eV (C-OH), 287.1 eV (C=O) and 288.7 eV (COOH) [21]. It is clearly shown that the C-N portion increases with increasing nitrogen doping concentration, i.e., 30.7 % for NGF-8.47, 22.7 % for NGF-1.03, and 24.0 % for NGF-2.22, respectively. Specifically, all NGFs have high amounts of hydroxyl groups (C-OH) and carboxy oxygen (C=O), which could promote the wettability of graphitic carbons in

electrolytes, resulting in better contact of electrode and electrolyte (Figs. S5d-S5f) [45, 46].

Fig. 3 High-resolution XPS test of NGFs. N1s spectra (a) NGF-1.03, (b) NGF-2.22 and (c) NGF-8.47, respectively. (d) The histogram of PD, PL and graphitic nitrogen contents in different NGFs.

The electrochemical behavior and performances are illustrated in Fig. 4. The CV curves (Fig. 4a) show a broad cathodic peak around 0.70 V (vs. K/K⁺) for all three NGF-x samples, which corresponds to the electrolyte decomposition and irreversible SEI formation. Cathodic peaks from 0.5 to 0.02 V are assigned to K⁺ intercalation and the formation of K-GICs at different stages [47]. During depotassiation, the broad and overlapped anodic peak around 0.43 V indicates high reversibility of the NGF electrode, ascribing to the corresponding deintercalation processes of K ions from graphite. There is an additional peak around 0.49 V for NGF-8.47 (Fig. 4b), assigning to the K⁺ storage

in nitrogen induced active sites [18]. However, the peak around 0.49 V is not obvious for NGF-1.03 and NGF-2.22, with a faint shoulder instead (Fig. 4b), probably due to their low N doping concentrations.

Fig. 4 Electrochemical tests of NGF-1.03, NGF-2.22 and NGF-8.47. (a) Cyclic voltammetry at 0.1 mV s^{-1} . (b) Selected range CV curves. (c) 1st charge and 2nd discharge of the galvanostatic profiles. (d) Rate performance evaluations, (e) cycling stability test at 40 mA g^{-1} and (f) Nyquist plots after 10 cycles' test of NGFs.

The charge/discharge profiles of the NGF-cells are displayed in Fig. 4c and Fig. S6. Three NGF electrodes store almost the same amount of K^+ ions during the first discharging (potasiation) process. Reversible specific capacities of 201.6, 212.3 and 231.4 mAh g^{-1} are obtained in the following charging (de-potasiation) process for NGF-1.03, NGF-2.22 and NGF-8.47, respectively. The highest reversible charge capacity of NGF-8.47 is owing to increased nitrogen induced holey active sites, resulting in highest ICE as well (59%). The long stage starts around 0.3 V (Fig. S6) attributed to K^+ intercalation [48]. During charge, K^+ extracts from graphite and KC_8 converts back to graphite, with a main platform around 0.25 V as shown in Fig. 4c. The 2nd platform

originates from K^+ desertion from nitrogen induced holey structures, which is much more notable for NGF-8.47 compared to NGF-1.03 and NGF-2.22 owing to higher doping concentration. Besides, NGF-8.47 exhibits more sloping charge-discharge curves compared to NGF-1.03 and NGF-2.22. This is attributed to its lowest degree of graphitization and highest disordered/defective structures [49, 50], as evidenced from XRD and Raman results. These features, on the other hand, account for the best cycling stability and highest reversibility.

Rate performance and cycling stability are further evaluated. The specific capacity of low N-doping samples decays rapidly from 226 and 213 to 36 and 87 mAh g^{-1} whereas it remains relatively high i.e., 112 mAh g^{-1} for NGF-8.47, with increasing the charge/discharge rate from 10 to 200 mA g^{-1} (Fig. 4d). This is ascribed to the enhancement of porosity, active site and conductivity with increased nitrogen contents and fast kinetics of K ion transportation in stable solid electrolyte interface and the electrode material [51]. Moreover, better cycling performance has been demonstrated for NGF-8.47 (Fig. 4e). For example, the capacity retention ratio of NGF-8.47 after 200 cycles at a current density of 40 mA g^{-1} is 86%, which is higher than that of NGF-1.03 (76%) and NGF-2.22 (80%). The improved cycling stability of NGFs with increased N-doping level is attributed to the reduced volume change and the increased chemical stability via nitrogen doping [24]. The electrochemical performance of undoped graphite foam was also evaluated for comparison (Fig. S7). As shown in Fig. S7a, GF exhibits weaker K^+ de-intercalation peak compared to NGF-1.03, indicating lower reversible capacity. This is also verified by galvanostatic charge/discharge curves (Fig. S7b), where the initial discharge and charge capacity, 324.8 and 192.2 mAh g^{-1} are achieved for GF. Besides, GF exhibits inferior rate capability. As shown in Fig. S7c, GF delivers a capacity of around 200 mAh g^{-1} at 10 mA g^{-1} . When the current density

increases to 200 mAh g⁻¹, the retained specific capacity is negligible (6 mAh g⁻¹). Fig. S7d demonstrates that GF has much poor cycling stability compared to NGF-1.03. After 70 cycles' test, only 101 mAh g⁻¹ capacity remained, giving a capacity retention of 31%. All these highlight the importance of N-doping for efficient K⁺ storage. Specifically, the much better rate and cycling performance of NGF-1.03 should be owing to enhanced conductivity and enlarged interlayer spacing after nitrogen doping.

In order to understand the underlying principles of improved performance, Nyquist plots are displayed in Fig. 4f. All of the Nyquist plots contain a depressed semicircle (high/medium frequency range) and a sloping line (low frequency range), which present the resistance of contact/charge transfer and ion diffusion impedance, respectively [52]. Here, R_s , R_{SEI} , R_{ct} and Z_W in Fig. 4f represent the intrinsic ohmic resistance (related with electrode, electrolyte and separator), the interphase contact resistance, the charge transfer resistance and ion diffusion impedance in electrode materials, respectively [22, 53]. It is obvious NGF-8.47 has the lowest charge transfer resistance (826.7, 466.4 and 393.1 Ω for NGF-1.03, NGF-2.22 and NGF-8.47), indicating the fastest intercalation kinetics [22]. Besides, the most vertical line of NGF-8.47 in low frequency indicates good capacitive behavior with fast diffusion of K⁺ in electrode materials. Meanwhile, the similar interphase resistances (34.9, 26.6 and 28.5 Ω for NGF-1.03, NGF-2.22 and NGF-8.47) reveal well-formed SEI layer in all the batteries, which is in agreement with CV curves and electrochemical impedance tests (Figs. 4a, 4f). All these results verify the significant effect of high concentration nitrogen doping on conductivity improvement.

In Fig. 5, we focus on the high/medium frequency range to diagnosis the kinetics during potassiation and de-potassiation of all NGF anodes during initial 2 cycles.[53] Fig. 5a exhibits the typical galvanostatic profile when acquiring Nyquist plots. Figs.

5b-j illustrates Nyquist plots acquired at different states of charge (SOCs) as indicated in Fig. 5a. The semicircles in high/medium frequency are prolonged and the Nyquist plots are flattened in low frequency at 0.6 V during first discharge for all NGFs, which could be endowed by the formation of SEI at this voltage, resulting in restricted K^+ ion diffusion and charge transfer [54]. As evidenced in second discharge process in Figs. 5d, 5g and 5j, there is no sharp variation at 0.6 V and the changing of resistance is progressive, which is an indicative of successful SEI formation during first discharge. Moreover, all batteries exhibit lower resistance during 2nd discharge compared to 1st discharge process. This may originate from the electrode activation process [55]. As we can observe from the Nyquist plots in Figs. 5c, 5f and 5i, NGF-1.03 and NGF-2.22 exhibit high contact/charge transfer resistances from 0.1 V to 0.3 V during charging. While for NGF-8.47, the semicircle becomes much smaller since charged to 0.3 V, which could be due to the facilitated K^+ deintercalation and enhanced electron transfer [21, 26], which is in line with charge profiles in Fig. 4c. Meanwhile, as the charge transfer resistance is greatly dependent on the amounts of K^+ intercalated, all batteries have a large semicircle at the fully discharged state (0.01 V) during 2nd discharging (Figs. 5d, 5g, 5j) [55].

Fig. 5 *In-situ* kinetic diagnosis during charge and discharge. (a) A typical potential vs. time profile collected during EIS test. Nyquist plots of (b-d) NGF-1.03, (e-g) NGF-2.22 and (h-j) NGF-8.47 at different states of charge (SOCs).

Previous investigations indicated that PD and PL nitrogen were correlated to the high capacity of N-doped carbon materials [18, 56]. Share et al. proposed that the high capacity of N-doped few-layer graphene is from the contribution of local pyrrolic N doping sites [18]. Xu et al. speculated that the capacity enhancement is related to both N-doping and carbon defects for their N-doped carbon nanofibers [56]. It is well known that the graphitic N doping results in the n-type graphene [57] and the binding between

graphitic N and K is weak, similar to Li in graphene [58]. Therefore, the graphitic N doping does not enhance the K-ion storage ability of graphene-like carbons. To better understand the nitrogen doping effect on electrochemical performances of N-doped graphite foam, we conducted the first-principles calculations. Different models of N-doped pore carbon with doping concentration of 2.4 at. % based on 6-atoms vacancy graphene were studied. With the defective graphene model C-V6 in Fig. S8a, we proposed different N-doping configurations, including graphitic N, pyrrolic N and pyridinic N (Figs. S8b-S8d). The formation energy of 6-atoms vacancy is calculated to be 5.029 eV (Table S2). Upon PD/PL nitrogen doping, the formation energy is reduced to 2.462 for PD and to 3.007 eV for PL, respectively. While for graphitic N doping, this value increases to 5.580 eV. This implies that the pyridinic/pyrrolic N doping is more favorable for defective structure formation. This was also verified by experimental results (Fig. 3d), where the percentages of both pyridinic N and pyrrolic N increase rapidly when the N doping level increases. Meanwhile, the amounts of mesopores are greatly increased (Fig. 2g). In other words, more pyridinic/pyrrolic nitrogen, more holey sites.

To further uncover the mechanism for improved K^+ storage capability, we studied the stable sites for K adsorption on porous graphene. As shown in Figs. 6a and Fig. S9a, the center of 6-atoms vacancy was found as the most stable site for K adsorption with high adsorption energy as illustrated in Table S3. With the increasing of concentration, K ions could be trapped nearby the hole firstly and then adsorbed on hollow sites of carbon plane, as shown in Fig. 6b. It was found that the site-3 and site-4 in Fig. S9a exhibit higher K adsorption energy than that of pristine graphene. The side view of high density K absorbed few-layer graphene is schematically illustrated in Fig. 6c. By comparing the adsorption energies of K on 6-atom vacancy with and without N-doping,

we found that different configurations (Fig. S9 and Table S3) do not increase the K adsorption obviously. It should be the induced pore rather than N-doping that contributes to the improvement in K^+ storage.

Fig. 6 Theoretical analysis of K adsorption and specific capacity of hole carbon structure with the N-doping. (a, b) Top view of single K adsorption and seven K atoms adsorption around pore in graphene with 6-atoms vacancy and doped pyridinic N (C-V6-N6) atomic structures. (c) Side view of the structure of high-density K adsorbed in few-layer C-V6-N6. (d, e) Top view of electron charge density distribution differences. (f) The relation between adsorption energy of K and specific capacity.

As shown in Fig. 6f, the calculated theoretical specific capacity is over 400 mAh g^{-1} with 8 K atoms absorbed (model, 41C+1N), where the adsorption energy is far below zero, indicating strong interactions. Here the interaction between K and pore carbon could be investigated by the distribution difference of electron charge density in real space. Figs. 6d, 6e represent the electron charge transfers from K to the nearby nitrogen and carbon atoms. Due to the Coulomb interaction, the transferred charge is localized, indicating the typical ionic bond characteristic between K and nearby carbon. It is also

noticed that the charges tend to be accumulated around carbon rather than nitrogen atoms, further revealing that it is the pore induced by nitrogen rather than nitrogen itself that increases the capacity. Thus, the pyridinic N and pyrrolic N lead to the high capacity of graphene foam by creating large amounts of porous structures.

4. Conclusion

In conclusion, it is the holey structures induced by the PD and PL nitrogen, rather than PD/PL itself that contribute to improved K^+ storage. In addition, the enlarged interlayer spacing ($\sim 0.346 \text{ \AA}$) via nitrogen doping is found to be favorable for efficient K^+ intercalation/de-intercalation. We also demonstrate improved conductivity which is beneficial for reduced charge transfer resistance and better rate performance. As a result, with the increase in the nitrogen doping concentration to 8.47 at. % (PD/PL nitrogen takes 89% out of all nitrogen content), we obtained a high initial Coulombic efficiency (59%), high reversible capacity (247 mAh g^{-1}) and superior cycling stability (89% retention after 200 cycles).

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