Free-standing N-doped hollow carbon fibers as high-performance anode for potassium ion batteries

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ABSTRACT A novel hierarchical architecture—N-doped hollow carbon fibers decorated with N-doped carbon clusters (NHCF@NCC)—was synthesized for high-performance anode material of potassium ion batteries (PIBs). The material is formulated with porous N-doped hollow carbon fibers as the backbone, which effectively shortens the diffusion length of potassium ion and increases the interface between the electrode and electrolyte. In addition, the N-doped carbon clusters attached on the hollow carbon fibers can provide abundant reactive sites. Specially, NHCF@NCC could form a free-standing electrode with a three dimensional interconnected conductive network owing to the ultrahigh aspect ratio. In this way, NHCF@NCC delivers an excellent electrochemical performance as free-standing anode materials of PIBs, exhibiting a high reversible capacity of 310 mA h g⁻¹ at a current density of 100 mA g⁻¹, a long cycling stability of 1000 cycles with negligible degradation, and a superior rate performance of 153 mA h g⁻¹ at a large current density of 2000 mA g⁻¹.

Keywords: potassium anode, N-doped hollow carbon fibers, N-doped carbon cluster, free-standing

INTRODUCTION

Potassium ion batteries (PIBs), as one of alternative energy storage devices, have been extensively studied due to the suitable working voltage from the standard electrode potential (−2.93 V vs. SHE) and the abundance of potassium source [1–5]. Research on anode electrode materials is one of the hotspots for PIBs [6–8]. Compared with other materials (alloy, conversion materials, and so on) [9–13], carbon materials have the merits of low price, environmental friendliness, stability and low redox potential [14–16]. Carbon materials with various structures have been researched for potassium ion storage, including carbon nanotubes [17], carbon nanofibers [18], carbon

quantum dots [19], and graphite [2,20]. These materials show excellent electrochemical properties, demonstrating potential in term of enhanced reversible capacity [21]. There are two different types of potassium ion storage in carbon materials [7]. One is that potassium ions intercalate into graphitized sheet layers, forming a stage 1 graphite intercalation compound [2,22,23], while the other is surface capacitive storage relying on the doped heteroatoms, functional groups and defects to adsorb potassium ions [24,25]. However, relatively low reversible capacity and depressed kinetics impede PIBs's further development [26–29]. Furthermore, the common slurry coating method for preparing electrode materials is tedious and mixed with binder and conducted agent, which cut down the electrical conductivity of electrode materials [30–32].

The two different forms of potassium ion storage (intercalation and adsorption) point the way of electrode material preparation. The target material should have many large layer spacing and active sites for the intercalation and adsorption of potassium ions to improve the reversible capacity and alleviate the large volume changes caused by potassium ion storage [33]. Carbon nanotubes are promising as the anode materials of batteries owing to their entwined web morphology [14,34]. Their hollow structure can provide large space for the volume change caused by potassium ion intercalation/deintercalation. Furthermore, heteroatom doping, which has been explored by many studies, is an effective method to chemically modify the surface of carbonaceous materials for increasing the active sites on the surface to increase the metal ion adsorption [35–37]. The heteroatom will improve the reactivity and electric conductivity, which is effective for lithium ion batteries (LIBs) [38–40]. However, due to the ultrahigh aspect ratio, carbon nanotubes

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possess a small effective specific surface area for electrolyte ion adsorption, resulting in a low capacitance capacity. The hollow carbon fibers not only have the advantages of carbon nanotubes, but also can effectively increase the actual specific surface area. Therefore, porous N-doped carbon fibers with hollow structure and nitrogen doping have been synthesized for conveniently adsorbing potassium ions due to the inherent chemical activity arising from the nitrogen incorporation. It is worth mentioning that N-doped carbon fibers are free-standing due to their entwined web morphology, which will reduce experiment steps and improve the energy density due to the merits of conducting pathway, mechanical flexibility, and structural integrity. Moreover, the doping nitrogen on carbon fibers is possible more efficient for electron transfer due to the larger electronegativity of nitrogen than carbon's (3.5 vs. 3.0, arbitrary units) [41,42]. What is more, N-doping also can enlarge the interlayer space of carbon materials, thus improving the potassium ion intercalation. And, the defects caused by N-doping may be suitable for the diffusion of alkali metal ions [43].

In this work, we designed a new type of hierarchical N-doping hollow carbon fibers with some unevenly distributed nitrogen-doped carbon clusters (NHCF@NCC) as the free-standing anode materials for PIBs. The anode materials are prepared through hydrothermal and vacuum annealing, with pyrrole as nitrogen source and MoO_3 nanowires as template. The porous N-doped hollow carbon fibers can effectively shorten the diffusion length of potassium ion and increase the interface between the electrode materials and electrolyte. The unevenly distributed N-doped carbon clusters will provide more active sites (mainly pyrrole-N) [44,45]. What is more, the hollow structure caused by MoO_3 nanowire template is beneficial to ion transfer. Based on these advantages, this novel NHCF@NCC shows excellent potassium ion storage performance as free-standing anode of PIBs, which has the merits of unique structure, good conductivity, and high chemical stability. Consequently, NHCF@NCC exhibits a high reversible capacity of 310 mA h g^{-1} at the current density of 100 mA g^{-1} , a long cycle stability of 1000 cycles with a negligible degradation, and a superior rate performance of 153 mA h g^{-1} at the current density of 2000 mA g^{-1} .

EXPERIMENTAL SECTION

Preparation of the MoO_3 nanowires

The MoO_3 nanowires were synthesized via a simple hy-

drothermal method by using ammonium molybdate as molybdenum source. In a typical procedure, 0.35 g ammonium molybdate was completely dissolved in a mixed solution (40 mL) (deionized water/ hydrogen nitrate=1/5, volume ratio) under ultrasonication. Then, the suspension was sealed into a 100-mL autoclave with a Teflon liner, and maintained at 200°C for 20 h. After being cooled to room temperature, the composite powders were obtained by centrifugation, and then washed with deionized water and ethanol several times. Finally, they were dried at 70°C for 12 h, and MoO_3 nanowires were obtained.

Preparation of the MoO_3 @PPy nanowires

The MoO_3 @PPy nanowires were prepared as follows. MoO_3 nanowires (0.2 g) were dispersed into 200 mL deionized water under ultrasonication to form a uniform solution. Thereafter, 0.1 mL of pyrrole was added into the above solution at 0°C in an ice bath and kept under this temperature for 12 h. Then the suspension was transferred into an autoclave with a Teflon liner, and maintained at 150°C for 48 h. After the polymerization of pyrrole on MoO_3 nanowires, the resulting precipitate was washed with deionized water and ethanol, and finally dried at 70°C for 12 h. The MoO_3 @PPy nanowires were obtained through annealing MoO_3 @PPy nanowires at 600°C for 2 h under argon flow with a heating rate of 5°C min^{-1} .

Preparation of the N-doped hollow carbon fibers

First, the MoO_3 @PPy nanowires were uniformly dispersed into 100 mL of ethanol. Then 20 mL of ammonium hydroxide was added into the solution under stirring. The MoO_3 reacted with the ammonia solution, $7\text{MoO}_3 + 6\text{NH}_3 \cdot \text{H}_2\text{O} \rightarrow (\text{NH}_4)_6\text{Mo}_7\text{O}_{24} + 3\text{H}_2\text{O}$ [46]. After 1 h, black free-standing electrode materials were collected through vacuum suction filtration and dried using freeze dryer for 12 h. Finally, the powder was annealed at 1000°C for 2 h under argon flow with a heating rate of 5°C min^{-1} . The mass loading was about 0.8 mg cm^{-2} , and the mass of work electrode materials was about 0.2–0.6 mg. The thickness of this free-standing electrode was about 0.5 mm. The electrodes materials were free-standing, and the amount was the average of three measurements using the electronic balance (precision of 0.01 mg). The amount of the electrode materials used was about 0.6 mg for various tests of the battery.

Material characterizations

The crystalline phase of the electrode materials was

characterized by X-ray diffraction (XRD, Bruker D8 ADVANCE, Cu K α). Scanning electron microscopy (SEM, Hitachi S-4800, 20 kV) and transmission electron microscopy (TEM, Titan G2 60-300 with image corrector) were used to observe the microstructure of the electrode materials. X-ray photoelectron spectroscopy (XPS, K-Alpha 1063, Thermo Fisher Scientific, England) was adopted to analyze the valence of elements. The surface area and pore size distribution of the electrode were analyzed by Brunauer–Emmett–Teller (BET, Quabrador SI-3MP). In addition, Raman spectra were studied using a Renishaw Raman Spectroscopy with 532 nm laser as excitation source.

Electrochemical measurements

The working electrodes were free-standing NHCF@NCC films through directly extracting using vacuum suction filtration. The PIBs were assembled in an Ar-filled glove box with the oxygen content and water content less than 0.5 ppm. The potassium-ion half cells were fabricated with a piece of free-standing NHCF@NCC (working electrode), potassium foil (counter electrode), glass fibers (separator), and electrolyte (4 mol L⁻¹ potassium bis (fluorosulfonyl)imide (KFSI) in 1,2-dimethoxyethane (DME)). The tests of galvanostatic charging/discharging process were performed using a battery testing system (Neware BTSCT-3008-TC 5.X, Shenzhen, China), with the potential range of 0.01–3.0 V. Cycle voltammograms (CVs) and electrochemical impedance spectroscopy (EIS) were tested by an electrochemical workstation (ArbinBT-2000).

RESULTS AND DISCUSSION

NHCF@NCC as the electrode materials of PIBs possesses three advantages for the potassium ion storage. First, the hierarchical structure of N-doped hollow carbon fibers and N-doped carbon clusters could accelerate the potassium ion diffusion and shorten the transfer pathways. Second, the doping of nitrogen atoms will enhance the wettability of the NHCF@NCC, which will improve the interface between the electrode and electrolyte to speed up the reaction rate [47–49]. Furthermore, different types of N-doping and oxygen-containing functional groups will offer active sites for the potassium ion adsorption. Third, the amorphous structure of carbon contains many two-dimensional (2D) graphite layer or 3D graphitic micro-crystallites. There are many irregular bonds or functional groups on the edges of the crystallites, which will provide more active sites for potassium ion adsorption [18,50–52]. So, the amorphous structure of NHCF@NCC is beneficial to the potassium ion adsorption. Schematic of the synthetic process of NHCF@NCC is depicted in Fig. 1. First, MoO₃ nanowires were prepared by a hydrothermal method, with smooth surface as shown in Fig. S1a. The diameter of the nanowires is about 200–400 nm. Then, pyrrole was uniformly coated on the surface of MoO₃ nanowires to form MoO₃@PPy nanowires *via* the polymerization of pyrrole monomers (Fig. S2a, TEM). As shown in Fig. S2b, the thickness of the polypyrrole (PPy) is about 20 nm. Further, the prepared MoO₃@PPy nanowires were annealed at 600°C for 2 h to form MoO₃@C (Fig. S1b, SEM). XRD patterns of the intermediate product are shown in Fig. S3. Many

Figure 1 Schematic illustration of the synthesis of NHCF@NCC.

Figure 2 (a) Photograph image, (b, c) TEM images, (d) HRTEM image, (e) elemental mapping, (f) XRD curve, (g) Raman spectra, (h) high-resolution N 1s XPS spectrum, and (i) high-resolution C 1s XPS spectrum of the NHCF@NCC.

small crystal particles of MoO_3 are impregnated in the nanowires at a certain temperature (Fig. S2c, d), resulting in the uneven-distributed N-doped carbon clusters. At last, the MoO_3 nanowire template was removed by ammonia to get the hierarchical NCNT@NCC.

The binder-free NHCF@NCC paper (Fig. 2a) with good flexibility and conductivity was prepared using vacuum filtration. Fig. 2b shows relatively uniform N-doped hollow carbon fibers decorated with some uneven wrinkles and small black spots, with the diameter of the fibers of ~ 430 nm (Fig. S4). In addition, we can also observe that the N-doped hollow carbon fibers have ultrathin tube walls as well as some holes on the wall. These unevenly distributed small black spots as shown in Fig. 2c confirm the existence of N-doped hollow carbon clusters that are

generated due to the cracking of MoO_3 bursting during annealing, which also can be seen in Fig. S1c. That is why there are few holes in the N-doped hollow carbon fibers, which will shorten the potassium ion diffusion and transfer path compared with those without defects. Furthermore, the uniform distributions of carbon and nitrogen are demonstrated by element mapping (Fig. 2e), which also proves the existence of N-doped carbon clusters. The disordered fingerprint-like structure of NHCF@NCC and the hollow fibers with a wall thickness of about 25 nm are revealed in the high-resolution TEM (HRTEM, Fig. 2d, Fig. S4).

That structure can provide large number of surface defects for the adsorption of potassium ions. And, the XRD curve of NHCF@NCC is exhibited in Fig. 2f, dis-

playing two broad peaks (at around 25° and 43°), which match with (002) and (101) planes of the disordered crystal structure [53–55]. Fig. 2g depicts the Raman spectra of the NHCF@NCC. The vibration of sp^2 -C in the 2D hexagonal lattice stands for the D-band peaks (1333 cm^{-1}), and the G-band at 1565 cm^{-1} represents the defect induced mode. The disordered structure of carbon materials can also be confirmed by the broad D-band and the intensity ratio of D-band to G-band ($I_D/I_G=1.06$), which agrees with the results of XRD and HRTEM [38]. The BET specific surface area (Fig. S5) was estimated to be $69.2\text{ m}^2\text{ g}^{-1}$, which could be preferred for high electrochemical performance [56]. High-resolution XPS spectra of N 1s and C 1s are exhibited in Fig. 2h, i, proving the doping of nitrogen and its types. In the high-resolution N 1s XPS spectrum, there are two peaks at around 399.29 and 401.49 eV, corresponding to pyrrolic N and graphitic N, exhibiting the nitrogen content in NHCF@NCC (about 3%, atomic ratio) [15,17]. Moreover, the nitrogen mainly exists in the form of pyrrolic N, which can provide fast potassium ion storage properties. There are five peaks in the high-resolution C 1s XPS spectrum, sp^2 -C band (284.7 eV), sp^3 -C band (284.9 eV), C–N/C–O band (285.7 eV), C=O band (287.3 eV), and O–C–N/O–C=O band (290.6 eV), suggesting five possible components. C–N/C–O band at 285.7 eV and O–C–N/O–C=O at 290.6 eV imply the existence of nitrogen in NHCF@NCC.

The electrochemical performance of the free-standing NHCF@NCC anode for PIBs is shown in the Fig. 3. Fig. 3a shows the typical CV curves of the NHCF@NCC anode. There is a large cathodic peak at 0.425 V at the first cycle, which can be attributed to the formation of the solid electrolyte interface (SEI) layer and the decomposition of electrolyte (including salts and solvents). In the next CV curves, there are cathodic peak at 0.69 V and anodic peak at 1.49 V, in which the small redox peaks at 0.69/1.49 V show a sign of pseudocapacitance [49,50,57]. From the third cycle, the shape of the CV curve does not change significantly. Such redox behaviors are also observed in the charge/discharge curves. The charge/discharge curves for the 3rd, 100th and 1000th are shown in Fig. 3b, and the first and second cycle curves are shown in Fig. S6. There is a low initial coulombic efficiency (ICE) for the first charge/discharge curve, which can be ascribed to the formation of SEI layer on the surface of the electrode materials, corresponding to the result of CV. One reason for the low ICE may be the hierarchical porous structure, where more contact interface between the electrode and electrolyte needs to form more SEI. And,

the most important reason is the decomposition of the salt (KFSI) and solvent (DME) in the electrolyte. The compatibility between FSI^- anions and K metal enables the formation of a stable SEI with abundant fluoride species. However, FSI^- anions will lead to the decomposition of KFSI because it is unstable to nucleophiles, superoxide, and hydroxide. The ICE could be improved through pre-potassiation [58,59]. As expected, the capacity becomes stable and reversible after the first cycle. In addition, the overlap of the charge/discharge curves between 100th and 1000th demonstrates the superior cycle stability.

As shown in Fig. 3c, the cycling stability of NHCF@NCC at 100 mA g^{-1} with a voltage range of 0.01–3.0 V was measured to further explore the electrochemical performance of the anode. After 1000 cycles, the capacity of NHCF@NCC is remained around 310 mA h g^{-1} with no loss, with the 12th cycle as the reference, revealing high cycling stability of the electrode material. The excellent cycling stability can be attributed to NHCF@NCC's special hierarchical porous structure and relatively high nitrogen doping. The porosity and hollow fiber characteristics will offer sufficient interface between the electrode and electrolyte to store potassium ions and can provide convenient channels for potassium ion transfer and diffusion. Due to the larger electronegativity of nitrogen than carbon, nitrogen doping will be more efficient for electron transfer, offering more reactive sites (mainly pyrrolic-N) [58]. In addition, the combination of nitrogen atoms with the carbon materials reinforces the interactions between the alkali metal ions and electrode, leading to the high reversible capacity and good cycling stability of the anode. Furthermore, defects induced by the pyrrole-N can provide many intercalation sites for potassium ions, thus improving the reversible capacity of PIBs. Interestingly, such defects-sites not only exist on the N-doped carbon nanotubes but also on the N-doped carbon clusters. It is worth mentioning that the NHCF@NCC shows exhilarated rate performance with the reversible capacities (Fig. 3d) of 301, 265, 218, 186, and 153 mA h g^{-1} , at current densities of 100, 200, 500, 1000, and 2000 mA g^{-1} , respectively (corresponding charge/discharge curves are shown in Fig. S7). The reversible capacity could be recovered to the previous capacity value when the current density turned back to the corresponding current value, which exhibits high stable cycling performance.

As we know, ICE, capacity retention ratio, cycle life and reversible capacity are critical electrochemical parameters of the electrode. As shown in the comparison of the above

Figure 3 Electrochemical performances of NHCF@NCC for PIBs: (a) first four consecutive CV curves in a voltage range of 0.01–3.0 V vs. K/K⁺ at a scan rate of 1.0 mV s⁻¹, (b) charge-discharge curves at current density of 100 mA g⁻¹, (c) cycling stability, (d) rate performance, and (e) a comparison of electrochemical performance of our work with other reports. The details are shown in Table S1 in the Supplementary information.

three criteria between NHCF@NCC and other carbon-based composite anodes (Fig. 3e), NHCF@NCC displays superior performance in capacity retention ratio, cycle life and reversible capacity. Specially, the capacity retention ratio is close to 100% even after 1000 cycles. Fig. S8a demonstrates that the hollow fiber structure could be well maintained in the NHCF@NCC anode after 50 cycles at 1000 mA g⁻¹. Even after 1000 cycles at 1000 mA g⁻¹ (Fig. S8b), the hollow fiber structure can almost remain unchanged.

To explore the storage mechanism of potassium ions, *ex-situ* XPS measurements at various states were conducted (Fig. 4a). For the pristine state, there are three peaks matching with C 1s (285 eV), N 1s (400 eV), and O 1s (534 eV), showing the distribution of elements in the pristine materials. Compared with the pristine state, two peaks emerge at around 293 eV (K 2p) and 378 eV (K 2s) in the discharge and charge state, demonstrating the storage of potassium ions during the discharge/charge process. As shown in Fig. 4b, based on the carbon peak

Figure 4 The XPS spectra at different states for PIBs: (a) full survey XPS, and (b) normalized XPS spectrum of C 1s and K 2p. Kinetics analysis of the electrochemical behavior of K^+ for NHCF@NCC: (c) CV curves at various scan rates, (d) determination of the b -values through the relationship between peak current and scan rate (e) Separation capacitive (blue) and diffusion-controlled (white) contribution of NHCF@NCC at 0.5 mV s^{-1} . (f) Contribution ratio of the capacitance and diffusion at different scan rates.

intensity, the peak intensity of the XPS spectrum was normalized to express the element content. The normalized intensity of K 2p at discharge process is higher than that of charge process, indicating that more potassium ions are adsorbed/intercalated on/into the anode materials during the discharge process. In addition, weaker peaks at charge process prove some residual potassium ions in the anode materials. Furthermore, *ex-situ* element mapping images were measured to understand the storage of potassium ions during cycling (as shown in Fig. S9). It can be found that there is only one peak located at 25.5° , and the small peak does not change during the discharge/charge process (as shown in

Fig. S10). It can be speculated that the main mechanism of this device is adsorption reaction by *ex-situ* XRD. According to the *ex-situ* element mapping, *ex-situ* XRD, and *ex-situ* XPS, the operating mechanism of PIBs is that the storage of potassium ions is mainly depending on the adsorption on the NHCF@NCC during the discharge/charge process.

The kinetic analysis was based on various CV curves. As shown in Fig. 4c, the shape of CV curves is similar with gradually obvious peaks caused by the N-adsorption of potassium ions. According to $i = av^b$, several processes contribute to the total stored charge, which could be calculated based on the CV data at various scan rates. In

the above formula, a and b are the adjustable parameters, i is the peak current and v is the scan rate. In particular, the electrochemical reaction indicates a total diffusion-controlled process at $b=0.5$. On the contrary, $b=1.0$ indicates a surface capacitive-controlled process. For the NHCF@NCC electrode, b was calculated as the slope with $b_{\text{cathode}}=0.87$ and $b_{\text{anode}}=0.94$, reflecting that the current at peak voltage is mainly surface capacitive-controlled (Fig. 4d). What is more, the contribution ratio of the surface capacitive-control can be calculated by separating the current response into diffusion-controlled and surface capacitive-controlled process by $i(V)=k_1v+k_2v^{1/2}$ (k_1 , k_2 are constants). As shown in Fig. 4e, the surface capacitive-controlled contribution of the NHCF@NCC electrode is 56% at the scan rate of 0.5 mV s^{-1} , with the diffusion-controlled contribution of 44%. Moreover, the capacitance contribution is further enhanced with the increasing scan rates, caused by their hierarchical structure, sheet, and high electric conductivity. In general, the main mechanism of potassium storage in this PIB is adsorption, accompanied by partial intercalation reactions. In addition, the reaction dynamics of the NHCF@NCC electrodes after different cycles were analyzed by EIS [60–62]. The pristine NHCF@NCC electrode and the same electrode after the 1st and 10th cycles at 500 mA g^{-1} were recorded, as presented in Nyquist plots (Fig. S11). The semicircle represents the charge transfer resistance (R_{ct}) and the sloping line represents Warburg impedance. After the first cycle, the R_{ct} drops by 44.1% from 2937 to 1642 Ω , indicating the evolution of SEI film. It increases slightly by 16.2% from the 1st cycle to the 10th cycle, illustrating the formation of a robust SEI film, which benefits the stable electrochemical performance.

CONCLUSIONS

In conclusion, the hierarchical NHCF@NCC was developed through a template method, which can be used as the free-standing anode materials for PIBs. Due to the hierarchical structure (fibers@clusters), porous and thin-wall, high electrode/electrolyte wettability, and active sites (defects and doping), the designed NHCF@NCC anode had superior electrochemical performance, especially long-term stability. The hierarchical structure could provide more channels and space for potassium ion storage and transfer while keeping structural integrity, thus being the main reason for the high stability. Remarkably, the NHCF@NCC anode also exhibited high reversible capacity, around 310 mA h g^{-1} after 1000 cycles with no loss of capacity compared with the third cycle. Moreover, because of the high electronic conductivity from the high

content of pyrrolic N, there was a good rate capacity with 153 mA h g^{-1} at a current density of 2000 mA g^{-1} . According to the quantitative analysis, the capacitive process plays a more important role for potassium ion storage than the diffusion process.

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Supplementary information Supporting data are available in the online version of the paper.

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氮掺杂空心碳纤维用作高性能钾离子电池自支撑负极材料

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摘要 本文报道了一种具有多级结构(氮掺杂团簇复合中空碳纤维)、高可逆容量的钾离子电池负极材料(NHCF@NCC)。该电极材料以多孔氮掺杂中空碳纤维为骨架,具有大比表面积,可有效地缩短钾离子的扩散距离,增加电极材料与电解质的接触界面。另外,附着在中空碳纤维上的不规则的氮掺杂团簇可以提供更多的反应活性位点。由于碳纤维高的纵横比,NHCF@NCC可形成三维连通导电网络的自支撑结构。以NHCF@NCC为自支撑无衬底负极的钾离子电池表现出优异的电化学性能,100 mA g⁻¹电流密度下可逆容量可达310 mA h g⁻¹,1000次循环后容量无明显衰减。当电流密度增加到2000 mA g⁻¹,该自支撑电极仍具有153 mA h g⁻¹的可逆容量,显示了优异的倍率性能。