A novel synthesis of Nb$_2$O$_5$@N-CNFM nanocomposite as anode material for superior sodium storage

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Abstract: The development of a novel anode material with excellent cycle performance is of great significance to the promotion of the sodium ion battery. Adopting the renewable material BC as raw material, Nitrogen-doped Nb$_2$O$_5$-three-dimensional porous carbon fiber network composite (Nb$_2$O$_5$@N-CNFM) is prepared by a low-cost approach in the paper. The in-situ growth of Nb$_2$O$_5$ nano-particles on the carbon fiber surface inhibits the agglomeration of particles. The porous structure of carbon fiber promotes ionic transfer. Meanwhile, the structure of pyridine nitrogen, which is formed by the doping of N atoms, further enhances sodium storage. After 1000 times of cycle under the current density of 2 A g$^{-1}$, the capacity of the Nb$_2$O$_5$@N-CNFM electrode is 79 mAh g$^{-1}$, its capacity retention increasing significantly, with great application prospect.

1. Preface
In recent years, lithium ion battery (LIB) has been widely applied in the mass market. However, with the arrival of electric vehicles, lithium’s ever-increasing cost and limited natural sources (0.006% in the crust) restrict the development of lithium ion batteries. Therefore, the next-generation novel technology with low cost and efficiency for energy storage is urged to be developed. Boasting a storage mechanism similar to that of LIB and low price, the sodium ion battery becomes an important field for the development of batteries. But as its radius (0.102 nm) is larger than that of the lithium ion (0.076 nm), many electrode materials widely applied in LIB are not ideal for sodium storage, in particular the fact that anode materials have become an impeding factor in the development of sodium ion batteries.

Among various metal oxides (SnO$_2$, TiO$_2$, Fe$_2$O$_3$ etc.), the interplanar distance of the orthorhombic Nb$_2$O$_3$ (001) is 0.39 nm$^{[1]}$, which is conducive to the rapid diffusion and storage of Na$^+$. Research also found that the orthorhombic Nb$_2$O$_3$ (T-Nb$_2$O$_3$) performed a quick pseudocapacitance response$^{[2]}$ within the potential range of 0.01-2V(vs. Na$^+$/Na), which will be appealing to the achievement of synchronous high energy density and power density. Due to its open internal architecture, extensive researches have been carried out on T-Nb$_2$O$_3$. The nano-particle of T-Nb$_2$O$_3$ prepared by Kim et al.$^{[3]}$ can reach specific heat of 400 F g$^{-1}$, while its low conductivity ($\approx 3 \times 10^{-6}$ S cm$^{-1}$)$^{[4]}$ restrict its further application. In addition, the formation of orthorhombic phase requires a high calcination temperature (>$600^\circ$C), leading to the agglomeration of nano-particles.

By morphological control (like thready form and fibriform etc.) or compounding with high-conductivity carbon materials (such as porous carbon, graphene etc.), there are effective methods...
to improve the performance of Nb$_2$O$_5$. Bacteria cellulose (BC) is a low-cost and renewable biomaterial. With a porous network structure, rich in functional groups like hydroxy, it is suitable as the precursor for carbon fiber. On the other hand, heteroatoms (N$^{[5]}$, S$^{[6]}$ etc.) doping can transform the surface structure of the material. These nonmetal elements have different electronegativity from that of carbon, which can affect the electron density configuration of carbon materials after bonding with C atoms, resulting in transformation of electronic conductivity. Wang et al. designed a three-dimensional nitrogen-oxygen double-doped carbon nanofiber electrode (NOC) to be applied in sodium ion batteries, rendering great cycle stability, with a high capacity of 545 mA h g$^{-1}$ after 100 cycles at 0.1 A g$^{-1}$.

Based on the modification ideas, BC is taken as carbon sources in the paper; when pyrolyzed in high temperature, three-dimensional carbon fiber network can be obtained, so as to prepare nitrogen-doped Nb$_2$O$_5$-three-dimensional porous carbon fiber composite (Nb$_2$O$_5$@N-CNF). Research is carried out on the sodium storage performance of the materials, and the storage mechanism of Na$^+$ is studied through structural and chemical surface analysis, providing a feasible approach to the application of Nb$_2$O$_5$-based materials in sodium ion batteries.

2. Materials and methods

2.1. Preparation of Nb$_2$O$_5$@N-CNF

The method for preparation is shown as Fig.1. First, clean the bacteria cellulose in deionized solution and clips it into small pieces. Then immerse BC in deionized solution of ammonium oxalate niobate hydrate and urea (c(C$_4$H$_4$NNbO$_9$.xH$_2$O)=0.1M, c(CH$_4$N$_2$O)=0.5M) and let it stand for 48 hours at room temperature. After that, freeze and dry the BC hydrogel and get the BC aerogel. At the end, in atmosphere of nitrogen, after calcination at 800℃ for 2h, the composite material Nb$_2$O$_5$@N-CNF is obtained. With low nitrogen content in C$_4$H$_4$NNbO$_9$, it is unlikely for ammonium ions to be kept during impregnation and calcination, hence without adding CH$_4$N$_2$O, the Nb$_2$O$_5$@CNF composite material is synthesized.

2.2. Physical characterization

The microscopic morphology of the sample is observed with a transmission electron microscope (TEM, JEOL JEM-2100F). The crystal structure is analyzed through Cu target Kα emitter X-ray diffraction (XRD, Rigaku Ultima IV). Thermogravimetric analysis (TGA Henven HCT-1 thermogravimetric analyzer) is adopted to determine the Nb$_2$O$_5$ content in the sample. ASAP-2020 tester is adopted to carry out the absorption and desorption of nitrogen and measure the specific
surface area of the sample. The chemical composition is determined by X-ray photoelectron spectroscopy (XPS, Perkin Elmer 5400 ESCA).

2.3. Electrochemical characterization
The CR2025 battery is applied in the experiment to perform the electrochemical test. The active material, Super-P and polyacrylic acid adhesive (PAA) are mixed as uniform slurry at a mass ratio of 8:1:1 in N methyl pyrrolidone (NMP) solvent. Assemble CR2025 batteries with 1M NaClO4/EC+DEC electrolyte (the volume ratio is 1:1, and 2% FEC is added). Tests of constant current charge and discharge, cycle and rate performance are conducted through the Land CT2001A battery test system. The electrochemical impedance spectroscopy is tested at the CHI-660E electrochemical workstation.

3. Result and discussion

3.1. Morphology and structure characterization
The morphology of Nb2O5@CNF and Nb2O5@N-CNF is characterized through TEM (Fig.2), whereby the carbon nano-fiber with continuous, long fiber structure can be seen, with the diameter of about 30-50 meter, among which a few Nb2O5 particles are scattered. The fact that these particles are closely connected to the carbon fiber may be caused by the growth and agglomeration of part of Nb2O5 at the conjunctions of carbon fiber during high-temperature calcination. Under large magnification, numerous Nb2O5 nano-particles of in-situ growth can be seen on the carbon fiber surface, with sizes controlled within 10-15nm and clear lattice fringes, which indicates that Nb2O5 boasts great crystalinity. The spacing of the neighboring crystal planes is 0.39nm and 0.31nm respectively, which is corresponding to the (001) and (180) crystal planes of T-Nb2O5 [7]. In general comparison, N doping has no specific impact on material morphology.

![Fig.2 The TEM photographs of (a)Nb2O5@CNF and (b) Nb2O5@N-CNF; the TEM photograph of (c) Nb2O5@CNF and (d) Nb2O5@N-CNF](image)

The XRD maps of BC-CNF, Nb2O5@CNF and Nb2O5@N-CNF are shown as Fig.3a. The corresponding (001), (180), (181) diffraction peaks of the Nb2O5@CNF and Nb2O5@N-CNF maps when 2θ=22.6°, 28.3° and 36.5° respectively are consistent with the standard maps of T-Nb2O5 (JCPDS: 30-0873) [8], which indicates the synthesis of pure T-Nb2O5. Although the prepared T-Nb2O5 is tiny nano-particle, due to its high phase formation temperature, its peak profile is sharp, with good crystalinity. Comparing XRD maps of Nb2O5@CNF and Nb2O5@N-CNF, the peak positions, profiles and half-peak width of each crystal planes are consistent, indicating that N coping won’t have impact
on the crystal phase of T-Nb₂O₅ but the carbon structure. In addition, the carbon content of Nb₂O₅@CNF is approximately 48.9wt.% according to thermogravimetric test (Fig.3b). Nitrogen’s isothermal adsorption and desorption curves of Nb₂O₅@CNF and Nb₂O₅@N-CNF are shown in Fig.3c, and the pore size distribution curve through DFT calculation is shown in the illustration. The adsorption and desorption curves of the two materials both show a specific IV-typed isotherm, and the specific surface areas of the Nb₂O₅@CNF and Nb₂O₅@N-CNF samples reach 314.6 m² g⁻¹ and 367.3 m² g⁻¹ respectively. Their pore size distribution is similar, both of which have micropore distribution; while Nb₂O₅@N-CNF has more micropores at 0.5nm and 1 nm. Such composites with large specific surface area and micropore structure can enlarge the contact area with the electrolyte, which is conducive to ion diffusion.

The chemical surface composition of the sample is further determined through XPS. From the whole pattern, except from the Nb 3d, C 1s and O 1s peaks of the two samples at 200, 280 and 520 eV, there is an obvious N 1s peak of Nb₂O₅@N-CNF at 400eV, proving successful N doping with the material. Calculation figures show the N atoms account for 2.81%. There are two main peaks at 209.7 and 206.9 eV in the high resolution spectrum of Nb, which are corresponding to the spin-orbit twin peaks of 3d₃/2 and 3d₅/2 in Nb, proving the existence of T-Nb₂O₅[9]. Conducting peak fitting to the N 1s spectrum, three peaks of N-6(pyridine nitrogen), N-5(pyrrole nitrogen) and N-Q(graphite nitrogen) can be respectively observed at the corresponding binding energy of 398.4eV, 399.7eV and 401.2eVpyrrole nitrogen[10]. These three binding forms all can enhance the electronic conductivity of carbon, in particular the fact that the p electrons of pyridine nitrogen and pyrrole nitrogen can provide electrons for the π conjugate system of carbon, increasing the defects and active sites on the surface of carbon materials, which improves the absorption capacity of ions.

Fig.3 (a) XRD spectrum, (b) thermogravimetric curve, (c) BET curve (d) XPS whole pattern of Nb₂O₅@CNF and Nb₂O₅@N-CNF, (e) XRS spectrum of Nb 3d, (f) XRS spectrum of N 1s in Nb₂O₅@N-CNF
3.2. Sodium storage performance characterization

The chemical state and structure of the anode material of sodium ion batteries have great impact on the electrochemical performance. On the one hand, the chemical state and morphology of carbon materials determine the formation of SEI film, affecting the irreversible capacity of batteries. On the other hand, the transportation channel of the active material will be determined by the porous structure of the anode material, which will affect the cycle performance. Fig. 4a is the cycle performance diagram of the electrode of Nb2O5@CNF and Nb2O5@N-CNCF at current density of 0.2 A g\(^{-1}\). The initial discharge capacity of Nb2O5@CNF and Nb2O5@N-CNCF is 312 and 331 mAh g\(^{-1}\). There is capacity fading at different levels of the two samples in the first 20 cycles during the cycle, which can be attributed to the generation of SEI film, the decomposition of electrolyte at the beginning of the cycle combined with certain instability in the structure of electrode materials, leading to continuous consumption of sodium ions and reduction of the initial capacity. After 200 times of cycle, the electrode of Nb2O5@N-CNCF can maintain a reversible capacity of 146mAh g\(^{-1}\), remaining 95.8% retention compared with the 20th cycle as well as a reversible capacity of 129mAh g\(^{-1}\) after 200 times of cycle. There is a similar cycle curve of the Nb2O5 electrode (Fig. 4b), but after 50 cycles its capacity remains only 86 mAh g\(^{-1}\), with 97% coulomb efficiency, due to its poor conductivity, large particle volume and no carrier support. Performing large current charge and discharge to the electrode at the current density of 2 A g\(^{-1}\) (Fig. 4c), after 1000 times of cycle the electrode capacity of Nb2O5@N-CNCF remains 79mAh g\(^{-1}\), while that of Nb2O5@CNF remains 58mAh g\(^{-1}\). The result indicates that the Nb2O5@CNF material can effectively stimulate the embedding/ejection process of Na\(^{+}\). This composite electrode with this structure can not only intensify the bonding of Nb2O5 nano-particles and BC-CNCF carriers, but also demonstrate great volumetric strain capacity.

To learn more about the improvement of electrochemical performance caused by N doping, measurement of electrochemical impedance spectroscopy of Nb2O5@CNF and Nb2O5@N-CNCF electrodes before cycle is carried out (Fig. 4d). Fitting the data, \(R_s\), \(R_{ct}\), \(Z_w\) represent ohmic impedance, charge transfer impedance and Warburg impedance respectively. The curve is composed of arcs in the high frequency region and slashes in the frequency region. Conclusion can be made from the figure that the introduction of nitrogen promotes charge transfer on the electrode-electrolyte interface, due to the small charge transfer impedance, 248.1 \(\Omega\) of Nb2O5@N-CNCF. After N atom doping, the sp2 hybridized C atoms are replaced to form the doping structure of pyridine or pyrrole, and the electronegativity of N is greater than that of C, changing the local charge density of carbon materials. Free electrons and hole carriers increasing by electron dislocation on carbon fiber, its electron transfer is enhanced.

![Fig.4 (a) the electrodes of Nb2O5@CNF and Nb2O5@N-CNCF (b) the cycle performance of the Nb2O5 electrode at the current density of 0.2 A g\(^{-1}\) (c) the cycle performance of the Nb2O5@CNF and](image-url)
Adopting the non-in-situ TEM and XRD to analyze the morphology and structure changes of Nb$_2$O$_5$@N-CNF electrode after the charge and discharge cycle, so as to perform research on its sodium storage mechanism (Fig.5). The charging product of Nb$_2$O$_5$@N-CNF electrode after 100 times of charge and discharge under the current density of 0.2 A g$^{-1}$ is shown in Fig.5a; the original fiber morphology of the recycled product is still remained. As the lattice structure of Nb$_2$O$_5$ nano-particle crystals on carbon fiber is destroyed, its original lattice fringe cannot be observed, which turns out to an amorphous structure; while a few NbO nano-particles with about 5nm diameter can be observed in the original Nb$_2$O$_5$ crystals (Fig.5b). Due to the conductivity of the generated byproduct NbO, electron transmission can be facilitated within the electrode, improving the conductivity of the electrode during the cycle, which serves as a key factor for the fact that the material demonstrates great cycle performance. By adopting the non-in-situ XRD to carry out analysis on the phase change before and after the initial charge and discharge of the Nb$_2$O$_5$@N-CNF electrode (Fig.5c), and there is clear crystal peak of T-Nb$_2$O$_5$ before the cycle. After 100 times' cycle of charge and discharge, the typical XRD peak of T-Nb$_2$O$_5$ is disappeared and still not recovered after charge, indicating that the crystal structure of T-Nb$_2$O$_5$ is damaged during ion de-intercalation, which confirms the result of non-in-situ TEM. On the basis of analysis above and previous studies[11], a sodium storage mechanism of the Nb$_2$O$_5$@rGO electrode is proposed (Fig.5d), where during the initial discharge, the embedding of Na$^+$ into Nb$_2$O$_5$ forms an amorphous phase Na$_x$Nb$_2$O$_5$ and part of Nb$_2$O$_5$ will be converted into NbO, while some Na$^+$ was stored in carbon micropores and on the Nb$_2$O$_5$ surface with a capacitating reaction. When charging to 3V, Na$^+$ will break out partially and form the amorphous phase Na$_y$Nb$_2$O$_5$.

Fig.5 non-in-situ (a) TEM photograph of Nb$_2$O$_5$@N-CNF electrode after 100 times of cycle under the current density of 0.2 A g$^{-1}$ (b) HRTEM photograph (c) non-in-situ XRD pattern (d) the reaction mechanism diagram of the sodium ion in the Nb$_2$O$_5$@N-CNF electrode

4. Conclusion
Adopting the renewable BC as raw material, the N-doped Nb$_2$O$_5$- three-dimensional porous carbon fiber network composite (Nb$_2$O$_5$@N-CNF) is prepared by a low-cost method, its sodium storage performance observed. With BC, it’s easy to get access to three-dimensional porous carbon fiber. The Nb$_2$O$_5$ nano-particles of 10-15 nm grow in situ on the surface of carbon fiber, restraining the agglomeration of the particles. The interconnected carbon fiber can accelerate electron transfer, with the transport of ions and electrolyte enhanced by the rich porous structure. After 200 times of cycle, the
Nb$_2$O$_5$@CNF electrode can maintain the reversible capacity of 129 mAh g$^{-1}$ under the current density of 0.2 A g$^{-1}$. N doping leads to more surface defects and active sites for carbon materials, which is conducive to the more secure modification of Nb$_2$O$_5$ on the carbon fiber surface. In addition, the formation of pyridine nitrogen and pyrrole nitrogen structures makes greater conductivity for carbon fiber with low degree of graphitization, which enhances the cycle performance of large current dramatically. The capacity of Nb$_2$O$_5$@N-CNF electrode after 1000 times of cycle under the current density of 2 A g$^{-1}$ is 79 mAh g$^{-1}$. These methods are conducive to the improvement of other electrode materials and the of the sodium ion battery.

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References
[1] Wang X, Li G, Chen Z, et al. (2011) High-Performance Supercapacitors Based on Nanocomposites of Nb2O5 Nanocrystals and Carbon Nanotubes. Advanced Energy Materials, 1: 1089-1093.
[2] Lim E, Jo C, Kim M S, et al. (2016) High-Performance Sodium-Ion Hybrid Supercapacitor Based on Nb2O5@Carbon Core-Shell Nanoparticles and Reduced Graphene Oxide Nanocomposites. Adv Funct Mater, 26: 3711-3719.
[3] Kim J W, Augustyn V, Dunn B. (2012) The Effect of Crystallinity on the Rapid Pseudocapacitive Response of Nb2O5. Advanced Energy Materials, 2: 141-148.
[4] Lin J, Yuan Y, Su Q, et al. (2018) Facile synthesis of Nb2O5/carbon nanocomposites as advanced anode materials for lithium-ion batteries. Electrochim Acta, 292: 63-71.
[5] Xu H, Ma L, Jin Z. (2018) Nitrogen-doped graphene: Synthesis, characterizations and energy applications. Journal of Energy Chemistry, 27: 146-160.
[6] Liu T, Li X. (2019) Biomass-derived nanostructured porous carbons for sodium ion batteries: a review. Materials Technology, 34: 232-245.
[7] Liao J, Tan R, Kuang Z, et al. (2018) Controlling the morphology, size and phase of Nb2O5 crystals for high electrochemical performance. Chin Chem Lett, 29: 1785-1790.
[8] Henry A, Le Vot S, Alauzun J G, et al. (2019) Electrochemical investigations of Nb2O5/carbon materials from filter paper, microfibrillated and bacterial cellulos by sustainable reductive mineralization. Electrochim Acta, 313: 478-487.
[9] Fu S, Yu Q, Liu Z, et al. (2019) Yolk-shell Nb2O5 microspheres as intercalation pseudocapacitive anode materials for high-energy Li-ion capacitors. Journal of Materials Chemistry A, 7: 11234-11240.
[10] Wang M, Yang Z, Li W, et al. (2016) Superior Sodium Storage in 3D Interconnected Nitrogen and Oxygen Dual-Doped Carbon Network. Small, 12: 2559-2566.
[11] Kim H, Lim E, Jo C, et al. (2015) Ordered-mesoporous Nb2O5/carbon composite as a sodium insertion material. Nano Energy, 16: 62-70.