Electrospun MoO₂@NC nanofibers with excellent Li⁺/Na⁺ storage for dual applications

Jiaojiao Liang, Xian Gao, Jing Guo, Changmiao Chen, Kai Fan and Jianmin Ma*

ABSTRACT MoO₂@N-doped C nanofibers (MoO₂@NC NFs) were synthesized by electrospinning with polyacrylonitrile as carbon source. The *in situ* formed MoO₂ nanocrystals are completely embedded in the carbon nanofibers, which can not only accelerate ion transition, but also act as a buffer to avoid the mechanical degradation of active material due to the volume changes during charge/discharge cycling. When used as the anode material for both Li/Na-ion batteries, the as-synthesized MoO₂@NC NFs displayed excellent Li⁺/Na⁺ storage properties. As the anode for Li-ion battery, the MoO₂@NC NFs display a high discharge capacity of 930 mA h g⁻¹ at a current density of 200 mA g⁻¹ for 100 cycles, and 720 mA h g⁻¹ at a current density of 1 A g⁻¹ for 600 cycles. Moreover, the discharge capacity of 350 mA h g⁻¹ could be realized at a current density of 100 mA g⁻¹ for 200 cycles for Na-ion battery.

Keywords: electrospinning, MoO₂, nanofibers, Li-ion batteries, Na-ion batteries

INTRODUCTION

In recent years, it has drawn much attention to develop high-performance energy storage devices, which can convert other energies into electric energy or store energy effectively. As one of effective energy devices, lithium-ion batteries (LIBs) have been widely used in portable electronics, and are being applied in electric vehicles (EVs) and hybrid electric vehicles (HEVs), owing to their excellent characteristics of high-energy density and long cycling life [1–3]. More recently, sodium-ion batteries (SIBs) have also attracted great attention as potential energy storage applications because of the low cost, abundant reserves and better safety of sodium [4–6]. However, they are facing the same challenge in exploring high-capacity anode materials for both LIBs and SIBs. To develop high-capacity anode materials for LIBs and sui-

table anode materials for SIBs, many efforts have been made to explore potential transition-metal oxide anode materials due to easy fabrication and low cost.

MoO₂, as a layered transition-metal oxide, has obtained intensive attention due to its good electrical conductivity and high theoretical capacity [7–10]. However, MoO₂ suffers from mechanical degradation owing to large volume variations during the ion insertion and extraction processes. This leads to the rapid decay of battery capacity. To solve this problem, a lot of MoO₂/carbon composites have been synthesized to overcome the volume change during charge/discharge processes, and improve the performance of MoO₂ electrodes effectively, including carbon matrix-embedded MoO₂, carbon-coated MoO₂, multiwall carbon nanotubes (MWCNTs)@MoO₂/C and reduced graphene oxide (rGO)-wrapped MoO₂ [11–14]. In addition, one-dimensional (1D) nanostructure can enhance the performance of Li-ion/Na-ion battery, through preventing the reunion of the active material, orienting and speeding up the electronic transmission and providing a large specific surface area [15–17]. Therefore, it is reasonable to develop 1D MoO₂/C composites as potential anode materials for LIBs and SIBs. Electrospinning technique is a conventional method for synthesizing 1D nanostructures [18–20]. The continuous 1D nanostructure can be applied to construct the interconnected network structure. The networks can not only well guide the transmission of charge but also afford a terrace for better interface in the active material and the current collector [21–24].

In this work, we successfully synthesized 1D MoO₂@N-doping C nanofibers (MoO₂@NC NFs) by electrospinning and subsequent heat treatment. The carbon of MoO₂@NC NFs could afford the MoO₂ nanocrystals short pathways for charge transfer, and accelerate Li/Na-ion diffusion. Moreover, MoO₂@NC NFs with the carbon matrix

School of Physics and Electronics, Hunan University, Changsha 410082, China

* Corresponding author (email: nanoelechem@hnu.edu.cn)

wrapping MoO_2 acted as a buffer layer to prevent the huge volume changes during charge/discharge process. The high discharge capacity reaches up to 930 mA h g^{-1} at a current density of 200 mA g^{-1} for 100 cycles, 720 mA h g^{-1} at a current density of 1 A g^{-1} for 600 cycles for LIBs. Furthermore, when used as the anode for NIBs, the $\text{MoO}_2@\text{NC}$ NFs could achieve 350 mA h g^{-1} at a current density of 100 mA g^{-1} for 200 cycles.

EXPERIMENTAL SECTION

Materials synthesis

$\text{MoO}_2@\text{NC}$ NFs were synthesized by electrospinning and subsequent heat treatment. In a typical process, 0.6 g polyacrylonitrile (PAN, $M_w = 150,000$, Sigma-Aldrich Co., Ltd., USA) was firstly dissolved in 7 g N,N -dimethylformamide (DMF) to form a homogeneous solution. Then, 3 mmol molybdenum acetylacetonate (Sigma-Aldrich Co., Ltd., USA) was added to the above solution with a magnetic stirring at 60°C for 6 h . Next, the blue mixture colloidal solution was drawn into an injection syringe equipped with a polytetrafluoroethylene (PTFE) tube. At the same time, the injection syringe was controlled by a peristaltic pump with a speed of 0.6 mL h^{-1} at a high voltage about 12 kV , the distance from the injector needle to the collecting plate was set to be 12 cm . After being gathered and vacuum dried at 60°C for 12 h , the precursor was pre-treated at 230°C in muffle furnace and then transferred to a tube furnace for annealing at 600°C with a heating rate of 1°C min^{-1} in Ar/H_2 ($8\% \text{ H}_2$). The NC NFs were obtained according the same procedure except without molybdenum acetylacetonate.

Materials characterization

The morphology and structural characterizations were observed using scanning electron microscope (SEM, Hitachi S4800), transmission electron microscope (TEM; JEOL 2010 with an accelerating voltage of 200 kV) and X-ray diffraction (XRD, Rigaku D/max 2500 diffractometer). The surface element composition of the samples was analyzed by X-ray photoelectron spectroscopy (XPS). The thermal gravimetric analysis of $\text{MoO}_2@\text{NC}$ NFs was processed on a thermogravimetric analyzer (TGA, TA company SDT Q600) with a heating rate of $10^\circ\text{C min}^{-1}$ in air from 30 to 700°C . Raman spectra of the samples were recorded by using Micro Raman Spectrometer (LabRAM HR Evolution, HORIBA).

Electrochemical measurements

To investigate the electrochemical performance of the as-

prepared samples, the anode materials of Li-ion /Na-ion batteries were prepared by the active materials ($\text{MoO}_2@\text{NC}$ NFs and NC NFs, respectively, $80 \text{ wt.}\%$) mixing with acetylene black ($10 \text{ wt.}\%$) and carboxymethylcellulose sodium (CMC, $10 \text{ wt.}\%$), and the Cu films were used as current collectors. Electrochemical properties of the as-prepared electrodes were measured using CR-2025 type coin cells, and metallic lithium/sodium plates were used as the counter electrodes. Celgard 2400 microporous polypropylene membranes were used as a separator of Li-ion batteries, and 1.0 mL L^{-1} LiPF_6 solution mixed ethylene carbonate (EC) and dimethyl carbonate (DMC) with 1:1 in volume, was used as the electrolyte of Li-ion batteries. And the glass microfiber filter (Whatman, grade GF/A) and 1.0 mL L^{-1} of NaClO_4 in a mixture of an EC and DMC solution (a volume ratio of 1:1) with 5% fluoroethylene carbonate (FEC) acting as additive were served for the separator and the electrolyte of Na-ion batteries, respectively. All of the coin cells were operated in a glove box. The electrochemical performance measurements were carried out at different current densities by Neware Battery Testing system, and the test voltage was between 0.001 and 3.0 V versus Li^+/Li (Na^+/Na). Meanwhile, cyclic voltammetry (CV) was performed in the same voltage window by using a CHI 660C electrochemical workstation with a scanning speed of 0.1 mV s^{-1} .

RESULTS AND DISCUSSION

The morphology and structures of the as-prepared $\text{MoO}_2@\text{NC}$ NFs are observed *via* SEM and TEM techniques, as shown in Fig. 1. The SEM image (Fig. 1a) displays that the $\text{MoO}_2@\text{NC}$ NFs have an average diameter of about $300\text{--}400 \text{ nm}$, and which is larger than that of NC NFs (about 200 nm , Fig. S1). Moreover, the surface of $\text{MoO}_2@\text{NC}$ NFs in TEM image (Fig. 1b) is smooth. From the high-resolution TEM image (HRTEM) (Fig. 1c), one can clearly observe that small amount of MoO_2 nanocrystals circled in white and disorder carbon layer in the margin of $\text{MoO}_2@\text{NC}$ NFs. More detailed information is given in Fig. 1d, which indicates that abundant MoO_2 lattices are distributed in the interior of carbon material. Additionally, as shown in Fig. 1d, it can be found that the crystal lattice distance of 0.337 nm for the as-prepared $\text{MoO}_2@\text{NC}$ NFs, which is corresponded to the lattice planes of MoO_2 (111).

The crystallinity and phase of $\text{MoO}_2@\text{NC}$ NFs and NC NFs are characterized by XRD, as shown in Fig. 2a. The as-synthesized $\text{MoO}_2@\text{NC}$ NFs are corresponding to the carbon (PDF card No.3-401) and monoclinic MoO_2 (PDF

Figure 1 (a) SEM image, (b) TEM image, (c and d) HRTEM images of the MoO₂@NC NFs.

standard card: 65-1273). The weak broad crystalline peaks of MoO₂@NC NFs indicate that the MoO₂ nanocrystals have particularly small sizes [25]. Fig. 2b shows the TGA curve of the MoO₂@NC NFs. In the TGA curve, one could observe that the lost weight of the sample appears after 350°C, which is ascribed to the oxidation of the carbon in the MoO₂@NC NFs. At the same time, the MoO₃ may be generated by the oxidation of MoO₂, with weight retention of 53.9%. Based on the above analysis, the content of the MoO₂ in MoO₂@NC NFs is confirmed to be about 47.9 %.

The structure of MoO₂@NC NFs is further characterized by Raman spectrum, as shown in Fig. S2. Two peaks at around 1351 and 1591 cm⁻¹ in the curve can be corresponding to the D-band of disordered carbon and the G-band of graphitic carbon, respectively [26]. The MoO₂@NC NFs were also surveyed by XPS (Fig. S3). The high-resolution XPS spectra of Mo 3d, C 1s, N 1s and O 1s are recorded, and further analyzed in Fig. 3. The peaks

of Mo 3d could be matched with four components (Fig. 3a), including two peaks at 228.48 and 232.53 eV of Mo⁴⁺ and two peaks at 232.34 and 235.62 eV of Mo⁶⁺, respectively [27,28], and the presence of Mo⁶⁺ is probably due to the oxidation of superficial MoO₂ in the MoO₂@NC NFs [10]. The peaks of the C 1s can be divided into four peaks (Fig. 3b). The main peaks at 284.41 and 284.49 eV in Fig. 3b can be corresponded to C=C and C-C [29,30], whereas the binding energy of 286.79 eV can be assigned to C=O [31]. In addition, the peak located at 285.29 eV corresponded to C-N bond can verify the presence of nitrogen in MoO₂@NC NFs [32]. The signal of N 1s could be obviously resolved into two peaks with binding energy of 398.28 and 399.86 eV (Fig. 3c), corresponding to pyridinic nitrogen and pyrrolic nitrogen [33,34], further confirming that the existence of nitrogen in MoO₂@NC NFs. It is well-known that the nitrogen-doped carbon material can enhance the electrical conductivity and accelerate the reaction speed of the carbonaceous composites [35–37]. The carbon containing pyridinic nitrogen can also improve the energy storage performance because of the free p-electrons in the outermost shell of the pyridinic nitrogen through absorbing Li⁺/Na⁺ [38,39]. The peaks of O 1s can be divided into three peaks, as shown in Fig. 3d. Among them, the two peak at 531.22 and 531.62 eV could be corresponded to C=O [40], whereas another peak centered at 530.3 eV can be assigned to Mo–O [41].

In this work, the MoO₂@NC NFs were firstly studied as the anode material for LIBs, and NC NFs were also conducted with the same procedure as a comparison. Fig. 4a displays the CV curves of MoO₂@NC NFs in the voltage range from 0.001 to 3.0 V at scan rate of 0.1 mV s⁻¹. During the first curve, the reduction peaks are detected at the range of 0.6–0.8 V and 0.01–0.4 V, respectively. Moreover, another obvious reduction peak is

Figure 2 (a) XRD patterns of MoO₂@NC NFs, NC NFs; and (b) TGA curve of the MoO₂@NC NFs.

Figure 3 XPS spectra of the MoO₂@NC NFs: (a) Mo 3d; (b) C 1s; (c) N 1s; (d) O 1s.

observed in the range of 1.0–1.4 V in subsequent curves. It might arise from the changing reaction from MoO₂ to Mo (Equation 1) and the conversion of monoclinic MoO₂ phase into the orthorhombic Li_xMoO₂ phase (Equation 2), respectively [8,42]. Subsequently, the reduction peaks of voltage platform at about 0.3 V disappear after the second cycle. This might be associated with the formation of solid electrolyte interface (SEI) films. Moreover, the oxidation peaks were discovered in each cycle in the range of 1.0–1.6 V, which is associated with the formation of the MoO₂ (Equations 3, 4) [43].

The cycling performance of the MoO₂@NC NFs and NC NFs electrodes is displayed in Fig. 4c, and the first discharge/charge capacities are 1429 and 1100 mA h g⁻¹ at 200 mA g⁻¹, respectively, with an initial Coulombic efficiency of 79%. The low Coulomb efficiency may be due to the formation of the SEI film and the presence of irreversible reaction in the first cycle. Obviously, the

discharge capacity of MoO₂@NC NFs electrode is significantly higher than that of the NC NFs electrode. The discharge capacities are about 930 and 450 mA h g⁻¹ at 200 mA g⁻¹ after 200 cycles for MoO₂@NC NFs electrode and NC NFs electrode, respectively. Moreover, the rate capability of the MoO₂@NC NFs electrode was investigated as showed in Fig. 4d. The average discharge capacities are 1020, 890, 797, 696, 596, 464, 291 and 680 mA h g⁻¹ at the different current densities of 100, 300, 500, 1, 2, 5, 10 and 1 A g⁻¹, respectively. Fig. 4e demonstrates the long-term cycling performance. When the current density is increased to 1 A g⁻¹, the discharge capacity is still 720 mA h g⁻¹ after 600 cycles and the Coulombic efficiency is close to 100%. By contrast, the lithium-storage performances of different MoO₂/carbon composites reported (Table 1), we can acquire that the as-synthesized MoO₂@NC NFs possess better cycling performance and higher discharge capacity. Besides, the electrochemical impedance analysis of MoO₂@NC NFs for LIBs before cycle and after 100th cycle at the current of 1 A g⁻¹, and the Nyquist plots are showed in Fig. S4. In Fig. S4, it could be observed that the semicircle in the high-frequency region becomes wider and the straight slope in the low-frequency region turns into gentle after

Figure 4 Electrochemical performance for LIBs: (a) CV curves at 0.1 mV s^{-1} ; (b) galvanostatic charge/discharge voltage profiles at 200 mA g^{-1} of $\text{MoO}_2\text{@NC NFs}$; (c) cycling performances of NC NFs and $\text{MoO}_2\text{@NC NFs}$ at 200 mA g^{-1} ; (d) rate capabilities of $\text{MoO}_2\text{@NC NFs}$; and (e) cycling performances of $\text{MoO}_2\text{@NC NFs}$ at 1 A g^{-1} .

Table 1 Comparison of lithium-storage performance of different MoO_2 /carbon composites

Materials	Current density (mA g^{-1})	Cycle number	Discharge capacity (mA h g^{-1})	Ref.
$\text{MoO}_2\text{/NC NFs}$	200/1000	200/600	930/720	This work
$\text{MoO}_2\text{-C hollow spheres}$	200	50	763	[8]
N-doped carbon/ MoO_2	100	100	1141.8	[28]
$\text{MoO}_2\text{/N-doped CFs}$	500	500	840	[44]
Porous $\text{MoO}_2\text{@C}$	100/1000	50/850	1442/443.8	[43]
Graphite oxide- MoO_2	200/1000	80/100	754/584	[26]
$\text{MoO}_2\text{/carbon hollow spheres}$	500	200	580	[45]
Graphene oxide/ MoO_2	1000	100	431	[46]
$\text{MoO}_2\text{@C}$	500	140	861	[47]
Carbon-coated MoO_2	80	60	1113.3	[12]
$\text{MoO}_2\text{/N-doped graphene}$	100	60	785	[48]

Figure 5 Electrochemical performance for SIBs: (a) CV curves at 0.1 mV s^{-1} and (b) galvanostatic charge-discharge voltage profiles of MoO₂@NC NFs at 100 mA g^{-1} ; (c) cycling performances of NC NFs and MoO₂@NC NFs at 100 mA g^{-1} ; (d) rate capabilities of MoO₂@NC NFs.

the cycle. This indicates that the charge-transfer and lithium ion diffusion resistance change during the cycle. These results manifest the outstanding electrochemical performance of MoO₂@NC NFs as potential anode for LIBs.

The electrochemical performances of MoO₂@NC NFs and NC NFs as anode for SIBs were also studied. Fig. 5a shows the CV curves of MoO₂@NC NFs for the initial three cycles at a sweep speed of 0.1 mV s^{-1} in the range from 0.001 to 3.0 V. The broad peak of reduction voltage in the range of 0.001–0.4 V and 0.75–0.85 V might be associated with the formation of the SEI film in the initial discharge cycle and the conversion reaction from MoO₂ to Mo (Equation 5). This is similar to that of LIBs [8], as well as the potential of sodium embedded in MoO₂ closes to MoO₃ at $\sim 0.8 \text{ V}$ [49]. However, there was no other redox peaks in the voltage range of 1–3 V. This is probably because the formation of Na_xMoO₂ was not found and the insertion of Na in MoO₂ did not appear. The repetition redox peaks are observed at 0.8 V(reduced)/0.68 V(oxidized), and maintain the invariability with the subsequent two cycles (2nd and 3rd cycle), corresponding to the CV curves of MoO₂/GO for sodium-ion batteries

(Equations 5, 6) [50].

Fig. 5b shows the galvanostatic discharge/charge voltage profiles of MoO₂@NC NFs for SIBs at 100 mA g^{-1} . The low Coulombic efficiency in 1st cycle could be attributed to the formation of SEI film in the initial charge/discharge process. In Fig. 5c, the MoO₂@NC NFs can realize the discharge capacities of 350 mA h g^{-1} at a current of 100 mA g^{-1} after 200 cycles, whereas the discharge capacities of NC NFs is 220 mA h g^{-1} . Moreover, the rate performance of the MoO₂@NC NFs at various current densities is displayed in Fig. 5d. The average discharge capacities of 431, 372, 348, 329, 299, 260, 217 and 372 mA h g^{-1} are achieved at the current density of 50 mA g^{-1} , 100 mA g^{-1} , 300 mA g^{-1} , 500 mA g^{-1} , 1 A g^{-1} , 2 A g^{-1} , 4 A g^{-1} and 100 mA g^{-1} , respectively. When the current density is backed to 100 mA g^{-1} , the capacity of MoO₂@NC NFs electrode is rapidly restored to 372 mA h g^{-1} . Compared with the sodium storage performance of MoO₂/C composites reported (Table S1), the discharge capacity and rate performance of MoO₂@NC

NFs have been improved. Additionally, the Nyquist plots of MoO₂@NC NFs electrode are performed within the frequency range from 100 kHz to 0.01 Hz for SIBs before cycle and after 100th cycle at a current density of 100 mA g⁻¹, as shown in Fig. S5. The diameter of semi-circle relating to the charge transfer resistance is larger than that of MoO₂@NC NFs. And the gradients of straight line are correlated with Warburg impedance maintaining approximately invariability with that of MoO₂@NC NFs before cycling. These data indicate that the MoO₂@NC NFs exhibit the long cycling stability and remarkable rate performance for SIBs.

The excellent performance of MoO₂@NC NFs for Li-ion/Na-ion batteries indicates that the MoO₂@NC NFs are promising anode materials. This can be ascribed that the MoO₂ nanocrystals of MoO₂@NC NFs are completely imbedded in the NC NFs, which could promote electronic transmission and the outer layer of carbon material prevents the volume expansion during charge/discharge processes. Moreover, the existence of nitrogen and partial graphitization of carbon in the MoO₂@NC NFs could improve the conductivity of the material. Additionally, 1D nanofiber could also accelerate ion diffusion of the electrodes to enhance energy storage performance.

CONCLUSIONS

In summary, we successfully fabricated the MoO₂@NC NFs for LIBs and SIBs. When used as the anode materials for LIBs, the reversible capacities of the MoO₂@NC NFs were 930 mA h g⁻¹ for 100 cycles and 720 mA h g⁻¹ for 600 cycles at the current density of 200 mA g⁻¹ and 1 A g⁻¹, respectively. When used as anode for SIBs, the discharge capacity of the MoO₂@NC NFs was 350 mA h g⁻¹ at the current density of 100 mA g⁻¹ after 200 cycles. There are several possible reasons for superior energy storage performance of MoO₂@NC NFs. First, MoO₂ nanocrystals are all wrapped in carbon matrix of MoO₂@NC NFs and carbon matrix as a buffer layer to prevent mechanical degradation of MoO₂ nanocrystals because of volume variations during charge/discharge processes. Secondly, the nitrogen doped carbon nanofibers can improve the electrical conductivity of the MoO₂@NC NFs, and provide short pathways to electron-transport. Finally, the 1D structure of MoO₂@NC NFs can accelerate Li/Na-ion diffusion of the electrodes.

Received 27 July 2017; accepted 12 September 2017;
published online 26 October 2017

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Acknowledgements This work was supported by the National Natural Science Foundation of China (51302079).

Author contributions Liang J and Ma J designed the project. Liang J performed the main experiments. Gao X and Chen C put forward valuable suggestions. Guo J is responsible for the characterization of materials. Gao X and Fan K helped with the experiments. Liang J and Ma J analyzed the data and wrote the manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

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

Jiaojiao Liang is a PhD candidate in the School of Physics and Electronics, Hunan University. Her current research focuses on the synthesis of nanomaterials and their applications in lithium-ion and sodium-ion batteries.

Xian Gao is an undergraduate student at Hunan University. His current research is focused on the synthesis of nanomaterials and the preparation of devices.

Jianmin Ma is an associate professor in Hunan University, China. He received his BSc degree in chemistry from Shanxi Normal University in 2003 and PhD degree in materials physics and chemistry from Nankai University in 2011. During 2011–2015, he conducted the research in several overseas universities as a postdoctoral research associate. His research interest focuses on the synthesis of nanostructured materials, electrochemical storage devices, electrocatalysis, and gas sensors.

具有双重优异储锂/钠性能的电纺 $\text{MoO}_2@\text{C}$ 纳米纤维

梁娇娇, 高显, 郭景, 陈昌淼, 樊凯, 马建民*

摘要 以聚丙烯腈(PAN)作为碳源, 利用静电纺丝方法成功合成了二氧化钼/氮掺杂碳纳米纤维($\text{MoO}_2@\text{NC NF}$)。制备 $\text{MoO}_2@\text{NC NF}$ 过程中, 原位形成的 MoO_2 纳米晶体被完全嵌入碳纳米纤维, 不仅能加速电子转移, 而且还作为缓冲层, 避免在充/放电循环过程中由于体积变化引起活性材料在碳纳米纤维中机械降解。当 $\text{MoO}_2@\text{NC NF}$ 材料用作锂/钠离子电池的负极材料时, 展示出极好的储锂/钠性能。作为锂离子负极材料, $\text{MoO}_2@\text{NC NF}$ 在电流密度为 200 mA g^{-1} 的条件下, 经过100次循环后容量为 930 mA h g^{-1} ; 当电流密度为 1 A g^{-1} , 其600次循环后容量为 720 mA g^{-1} 。 $\text{MoO}_2@\text{NC NF}$ 用作钠离子负极材料, 在电流密度为 100 mA g^{-1} 的条件下, 经过200次循环过程后, 其容量稳定在 350 mA h g^{-1} 左右。