



# Negative electrode materials of molybdenum nitride/N-doped carbon nano-fiber via electrospinning method for high-performance supercapacitors

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## ABSTRACT

To widen the practical application of supercapacitors in acid electrolyte, carbon/molybdenum nitride (C/Mo<sub>x</sub>N) nanofibers are synthesized via combination of electrospinning method and thermal treatment in mixed gas atmosphere of N<sub>2</sub> and NH<sub>3</sub>. When the mass fraction of ammonium molybdate of 1.13 wt.% is added in the precursor mixture solution, as-prepared C/Mo<sub>x</sub>N composite shows the nanofibers of about 200 nm diameter with Mo<sub>x</sub>N nanoparticles uniformly embedded in the N-doped carbon substrate, and delivers a specific capacitance of 251 F g<sup>-1</sup>. Three types of supercapacitor devices of PANI||C/Mo<sub>x</sub>N, AC||C/Mo<sub>x</sub>N and C/Mo<sub>x</sub>N||C/Mo<sub>x</sub>N are configured in acid electrolyte. The asymmetric supercapacitor of PANI||C/Mo<sub>x</sub>N shows a maximum energy density of 14.1 Wh kg<sup>-1</sup> and power density of 312 W kg<sup>-1</sup>, which was larger than those of AC||C/Mo<sub>x</sub>N device (12 Wh kg<sup>-1</sup>, and 325 W kg<sup>-1</sup>) and symmetric supercapacitors of C/Mo<sub>x</sub>N||C/Mo<sub>x</sub>N device (4.51 Wh kg<sup>-1</sup>, and 250 W kg<sup>-1</sup>). The C/Mo<sub>x</sub>N||C/Mo<sub>x</sub>N device exhibits good cycle life of specific capacitance retention of 78.6% at 2 A g<sup>-1</sup> after 15,000 cycles.

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## 1. Introduction

Supercapacitors have been paid much more attention in the past decades due to its high power density, and long cycle life compared to batteries (Li ion battery, Ni-MH battery, Lead acid battery et al.), which could bridge the power/energy gap between traditional dielectric capacitors and batteries/fuel cells [1–7]. Generally, supercapacitors, same as other energy storages, consist of electrode materials (positive and negative materials), separator, and other parts. Among these, electrode materials play a critical role for supercapacitors' performance.

Generally speaking, according to energy storage mechanism, electrode materials are divided into two categories. Carbon materials are mainly based on an energy storage mechanism of electric double layer capacitors (EDLCs), containing activated carbon, carbon fibers [8], carbon nanotubes [9], porous carbon [10] and

heteroatom (N, S, B, P)-doped carbon [11–16]. Electrode materials are on the basis of pseudocapacitors energy storage mechanism, including metal oxides such as Mn-based [17,18], Ni-based [19–21], Co-based [22–28], Mo-based [29] and V-based [30,31], metal nitrides [32–35] such as vanadium nitride (VN), molybdenum nitride and titanium nitride (TiN), conducting polymers [36] such as polyaniline (PANI) [37–40] and polypyrrole (PPy) [41]. Compared with carbon materials, pseudocapacitive electrode materials, in general, exhibit a high specific capacitance but lower cycle stability.

Among pseudocapacitive electrode materials, most of them like metal oxides/nitrides are always applied in alkaline or neutral aqueous electrolyte, and not appropriate for acid aqueous electrolyte, which offers few options and limits the practical application of the electrode materials in acid electrolyte. Molybdenum nitride is just stable in acid solution, which would widen the range of application in acid electrolyte. J. Liu et al. reported single-crystalline molybdenum nitride nanobelts, which exhibited a specific capacitance of 160 F g<sup>-1</sup> with lower decay of 9% after 1000 cycles [42]. Zhang and Kong et al. prepared molybdenum nitride intermetallic material which showed satisfying pseudocapacitance of 171 F g<sup>-1</sup> with excellent cycling stabilities at current density of 1 A g<sup>-1</sup> in acid

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electrolyte [43]. Y. Xie et al. synthesized  $\text{MoN}_x$  with the capacitance of  $174.8 \text{ F g}^{-1}$  at  $1.5 \text{ A g}^{-1}$  and high rate capability with 93.8% specific retention after 1000 cycles [44]. Shah et al. prepared  $\text{Mo}_2\text{N}$  showed  $202 \text{ F g}^{-1}$  with nearly 100% specific retention after 1000 cycles [45]. However, the electrochemical performance, especially the specific capacitance of molybdenum nitride needs to be further enhanced to meet the practical usage.

It has been proposed that combining electrochemical active materials with carbon materials could largely enhance the supercapacitive performance, such as VN quantum dot/nitrogen-doped microporous carbon nanofiber [46], VN/nitrogen-doped graphene composite [47], ultra-small VN quantum dots embedded in porous carbon [48], and hybrid  $\text{MnO}_2$ /carbon nanotube-VN/carbon nanotube supercapacitors [49]. In this work, the carbon/ $\text{Mo}_x\text{N}$  nanocomposite was prepared in order to increase the dispersion of nano- $\text{Mo}_x\text{N}$  in the carbon materials and thus enhance the sufficient utilization of the active materials. The electrode active materials  $\text{Mo}_x\text{N}$  were fabricated and embedded into nanofibers by electrospinning and thermal treatment process. Electrospinning method is one of effective methods for preparing 1 D fiber structure, such as  $\text{NiCo}_2\text{O}_4$  nanofibers [50],  $\text{V}_2\text{O}_5$  nanofibers [51], and carbon nanofibers [52,53]. And polyacrylonitrile (PAN), with good stability, mechanical strength and high carbon yield, has been widely used as one important precursor to obtain carbon fibers [54,55]. Ammonium molybdate as Mo source was added to electrospinning solution, which contained PAN as carbon source, to combine nanoparticles with nanofibers for supercapacitor. Moreover, different amount of ammonium molybdate from 0.57 to 1.68 wt.% was mediated for controlling  $\text{Mo}_x\text{N}$  content and dispersion embedded into carbon nanofibers. The as-prepared negative electrode material C/ $\text{Mo}_x\text{N}$  exhibited a high specific capacitance of  $251 \text{ F g}^{-1}$ . Besides, the symmetric supercapacitor device and asymmetric supercapacitor devices were assembled by using as-prepared C/ $\text{Mo}_x\text{N}$  as negative material, and showed maximum energy  $4.51 \text{ Wh kg}^{-1}$  and  $12.0 \text{ Wh kg}^{-1}$ , respectively.

## 2. Experimental

### 2.1. Chemicals

Polyvinylpyrrolidone (PVP, K90), ammonium molybdate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ ), acrylonitrile (AN), 2, 2-azobis(2-methylpropionitrile) (AIBN), and *N, N*-dimethylformamide (DMF) were purchased from *Sinopharm Chemical Reagent Co., Ltd.* AN was distilled under vacuum, and AIBN was recrystallized from ethanol prior to use.

### 2.2. Preparation of polyacrylonitrile (PAN)

Synthesis of PAN was referred to our previous literature [52,53]: Typically, monomer AN (19.2 g), initiator AIBN (0.056 g), and solvent DMF (60 mL) were added into a 150 mL round bottom flask, which was stirred at  $70^\circ\text{C}$  for 6 h in the water bath to obtain a transparent solution. Subsequently, the solution was cooled down to room temperature, precipitated in ethanol for three times and dried at  $40^\circ\text{C}$  under vacuum for 24 h to obtain the PAN product.

### 2.3. Preparation of electrospinning solution

As-prepared PAN (1.2 g), PVP (0.2 g), DMF (10 mL), and ammonium molybdate were mixed with vigorous magnetic stirring in a 25 mL round bottom flask at  $70^\circ\text{C}$  in a water bath until a homogeneous solution. The mass fraction of ammonium molybdate were mediated as 0.57, 0.85, 1.13, 1.41, and 1.68 wt. %, respectively.

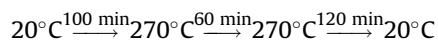
## 2.4. Preparation of C/ $\text{Mo}_x\text{N}$ samples

### 2.4.1. Electrospinning

The polymer nanofibers were prepared via electrospinning equipment. A culture dish with distilled water was put into placed on a steel plate, which was connected to the wire at room temperature to collect nanofibers. The electrospinning parameter was as follows: the voltage was in the range of 20–25 kV, and the distance between the needle tip and the water surface was about 6 cm, and the flow rate of electrospinning was about 1 mL/h.

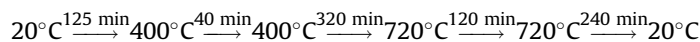
### 2.4.2. Pre-oxidization

The as-spun nanofibers were dried at  $60^\circ\text{C}$  and then pre-oxidized at  $270^\circ\text{C}$  for 60 min in air atmosphere. The pre-oxidized process was as follows:



### 2.4.3. Carbonation and ammonization

The as-pre-oxidized nanofibers were carbonated and ammoniated in the mixture gas atmosphere of nitrogen and ammonia gas with the flow ratio of 40:60 at  $720^\circ\text{C}$  for 120 min. The heat-treated process was as follows:



The obtained samples, loading different mass fraction of ammonium molybdate, were denoted as C/ $\text{Mo}_x\text{N}$ -0.57%, C/ $\text{Mo}_x\text{N}$ -0.85%, C/ $\text{Mo}_x\text{N}$ -1.13%, C/ $\text{Mo}_x\text{N}$ -1.41%, and C/ $\text{Mo}_x\text{N}$ -1.68%, respectively. In addition, the pristine  $\text{Mo}_x\text{N}$  was also prepared at the same condition by using ammonium molybdate as a precursor.

## 2.5. Characterization

The morphologies were examined by scanning electron microscopy (SEM, JSM-6701) and transmission electron microscopy (TEM, TECNAI TF20). The crystal structures and compositions of the as-prepared samples were characterized by using X-ray diffraction (XRD, D/max-2400, Rigaku,  $\text{Cu K}\alpha$ ,  $0.154056 \text{ nm}$ ). X-ray photoelectron spectra (XPS) were recorded on a Perkin-Elmer PHI ESCA system.

### 2.6. Electrode preparation

The prepared active material (80 wt.%), conducting graphite (7.5 wt.%), acetylene black (7.5 wt.%), and poly(tetrafluoroethylene) (5.0 wt.%) were mixed and formed slurry in an agate mortar, which was coated on the stainless steel of geometric surface area of ca.  $1 \text{ cm}^2$  as current collector and pressed at 10 MPa for ca. 15 s. Finally, the electrode was obtained by being dried at  $80^\circ\text{C}$  for 12 h.

### 2.7. Electrochemical performance evaluation

The electrochemical evaluation was employed by three-electrode system including the as-prepared active material as work electrode, a platinum foil electrode as counter electrode, and a saturated calomel electrode (SCE) as reference electrode, respectively. Cyclic voltammetry (CV) and galvanostatic charging/discharging (GCD) measurements were tested in  $1 \text{ M H}_2\text{SO}_4$  aqueous solution. Electrochemical impedance spectroscopy (EIS) measurements were performed over a frequency in a range of  $0.01\text{--}10^5 \text{ Hz}$  at an amplitude 5 mV. Cycle stability was carried out by

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