Hierarchical Metallized Polyimide Fiber for Flexible Supercapacitors with Ultra-High Capacity

Houchao Zhan Division of Energy and Environments, Tsinghua Shenzhen International Graduate School Shenzhen, China zhc18@mails.tsinghua.edu.cn

Cheng Yang Division of Energy and Environments, Tsinghua Shenzhen International Graduate School Shenzhen, China yang.cheng@sz.tsinghua.edu.cn

Abstract—Flexible supercapacitors show promising application prospects for portable electronic devices. It has the advantage of being charged/discharged at high rate, which is attributed to the ion storage on the electrode surface. However, this storage mechanism also brings low energy density. To improve the capacitance of supercapacitors when the energy storage device is bent has always been an important challenge. Here, we coated nickel (Ni) on the electrospun polyimide (PI) fiber to form a conductive nickelnanofiber membrane (NNM). coated Α flexible supercapacitor with ultrahigh specific capacitance was prepared through employing the current collector of the surface-metalized NNM. PI fibers with excellent mechanical properties can guarantee good flexibility. Additionally, the electrospun PI fiber shows a large specific surface area, and it also shows a high electrical conductivity after metallization. After depositing manganese dioxide, the NNM@MnO₂ delivers both high capacity and power density (207.5 F/g at 50 mV/s). This hierarchical PI-based current collector is easily scaled up and exhibits excellent electrochemical performance, showing promising applications in the field of flexible supercapacitors.

Keywords—flexible supercapacitors, surface metallization, hierarchical PI fibers

I. INTRODUCTION

Wearable devices place high demands on flexible energy storage devices, and much importance is attached to supercapacitors due to their outstanding cycle stability[1]. However, the supercapacitor is limited by low capacity, as well as the capacity loss caused by the bending of flexible devices. On the basis of the energy storage principle of the supercapacitors, the energy density can be improved from the following two aspects. On the one hand, the electric double layer capacity of the electrode material can be improved by increasing the specific surface area. Chemically converted graphene sheets have been widely adopted in the supercapacitors[2]. Multilayered graphene films don't aggregate very easily, and a larger accessible surface area is achieved. Therefore, both capacity and power density of the assembled supercapacitor could be improved. On the other hand, pseudocapative materials are often involved, which can provide higher specific capacitance. Because some chemical reactions happen on the electrode surface of these materials, instead of only surface adsorption [3]. To compensate their weak electric conductivity,

Min Wang Division of Energy and Environments, Tsinghua Shenzhen International Graduate School Shenzhen, China wangmin17@mails.tsinghua.edu.cn Caiwu Liang Division of Energy and Environments, Tsinghua Shenzhen International Graduate School Shenzhen, China lcw17@mails.tsinghua.edu.cn

conductive addictives are prepared to improve capacitance by e.g. polypyrrole coating[4]. Manganese oxide is one of the excellent pseudocapacitive material[5]. By directional growth of birnessite on the surface of manganese dioxide, the pseudo-capacitance of these manganese-based electrode materials with a core-shell structure can also be greatly improved[6]. In addition, the laser-induced MoS₂ material that forms the 1T phase can exhibit a large capacity and good cycling performance at high cycling speeds[7]. In addition to improving the intrinsic electrochemical performance of the electrode materials, some integrated energy storage modules have been developed. The cathode, anode, and separator in these devices are integrated, which could reduce the proportion of inactive materials and increases the overall energy density[8].

In order to obtain mechanically flexible devices, flexible self-supporting skeletons that often play the role of current collectors are also essential. Various carbon materials have developed as flexible substrates, been including graphene[9], carbon nanotubes[10], carbon cloth[11]. At the same time, some metal-based frameworks with high conductivity and large specific surface have also been developed[12]. Although there has been a lot of works on electrode materials and skeleton manipulations, it is still far away from the commercial application of flexible energy storage devices, and it still has great challenges for supercapacitors to present a higher and better energy storage capacity under the premise of ensuring good flexibility of the supercapacitor.

Here, by designing a flexible skeleton with high electrical conductivity and specific surface area, and loading high-performance electrode materials on it, we developed a scalable method for preparing high-capacity flexible supercapacitors in batches. After magnetron sputtering a layer of nickel on a reticular polyimide (PI) membrane film prepared by electrospinning, a layer of nickel is electrodeposited to prepare a flexible current collector substrate. These preparation methods are close to industrial production lines and are easy to achieve large scale production. The prepared NNM has large specific surface area, excellent mechanical properties, and high electric conductivity; It is very suitable for being a current collector of supercapacitors. MnO₂ is loaded on this substrate as cathode materials. And a high capacitance of 207.5 F/g at 50 mV/s was achieved, which could be ascribed to the synergy of a large specific surface and pseudo-capacitance properties at the same time. In addition, after 5000 cycles, a capacitance retention of 87.4% was maintained. Activated carbon was loaded on the NNM as the anode. The supercapacitor devices assembled with NNM@MnO₂ and NNM@AC could be bent to 180°, showing good flexibility. This method provides a new way of preparing high-capacity flexible supercapacitors in large quantities, which is instructive for future applications in this field.

II. EXPERIMENTAL SECTION

A. Preparation of nickel-coated nanofiber membrane (NNM)

Electrospinning method was employed to prepare the poly(amic acid)(PAA) nanofiber membrane. The electrospinning distance and speed was 20 cm and 0.1 mm/min separately, with an applied voltage of 18 kV. After being removed from the aluminum foil substrate, the PAA nanofiber membrane was then maintained at 300 °C for 30 minutes at a flow rate of 5 °C/min, and the polyimide (PI) nanofiber membrane was prepared through imidization. After magnetron sputtering a layer of Ni on the PI nanofiber membrane, a layer of Ni was deposited by electrochemical deposition. The plating solution contains 0.65 M H₃BO₃, 0.17 M NiCl₂·6H₂O, 1 M NiSO₄·H₂O, and 0.2 g/L sodium dodecyl sulfate. And the ammonia water was then dropped into the solution to adjust the pH to 4.8. Afterwards, a current of 5 mA/cm² with a power supply was applied to the electrode for 10 minutes to obtain a Ni-coated nanofiber membrane (NNM).

B. Preparation of NNM @ MnO₂ and NNM @ AC

A layer of MnO_2 was electrochemically deposited onto the NNM in a dual-electrode system to prepare the NNM@MnO₂ electrode, and the titanium platinum was employed as the counter electrode. The formulation of the electrochemical deposition solution includes 0.1 M manganese acetate. The current density of the electrochemical deposition is 5 mA/cm², and the deposition time is 2 minutes. The production was washed with deionized water for three times, and then placed in a vacuum oven at 60 °C overnight.

Activated carbon (AC), conductive carbon black and PVDF binder are mixed and ground according to the mass ratio of 7:2:1, and then the mixed powder was dissolved in NMP and stirred for more than 12 hours. Afterwards, the slurry was brushed on the current collector skeleton. Subsequently, it was washed and dried.

C. Material characterization and electrochemical characterization

The changes in the surface morphology and microstructure of the electrode material was analyzed employing the scanning electron microscopy (SEM). Cyclic voltammetry (CV) curves are tested to characterize the capacity and the rate performance. And galvanostatic charge-discharge (GCD) are tested to evaluate the reversibility and other electrochemical performance. The instrument employed in both CV and GCD testing is VMP3 working station (Bio-Logic) tester. The EIS was tested by the instrument of CHI 610E to characterize the internal impedance. The frequency range was set from 100 kHz to 0.01 Hz, and the potential

amplitude is 5 mV. Unless specifically mentioned, the electrochemical tests were conducted inside a threeelectrode system, which contains 0.5 M NaSO₄, platinum, and saturated calomel electrode, functioning as the electrolyte, the counter electrode, and the reference electrode separately. The potential range of the NNM@MnO₂ electrode was set from 0 V to 0.8 V, and the potential window of NNM@MnO₂//NNM@AC is 0-1.6 V. The specific capacity is calculated as the following formula:

$$C = \frac{\int i(V)dV}{m \cdot v \cdot \Delta V}$$

Where C (F/g) is the mass specific capacity of the electrode, ΔV (V)is the testing potential range of the supercapacitor, and "m" is the load of the active material, and "v" is the scanning speed.



Fig.1 Schematic diagram of the preparation process of the NNM@ MnO_2 cathode and the NNM@AC anode.

III. RESULTS AND DISCUSSIONS

The preparation process of the NNM@MnO₂ cathode and NNM@AC anode of the asymmetric supercapacitor is shown in Fig.1. After magnetron sputtering Ni on the electrospun PI nanofiber film, a layer of Ni is electrochemically deposited to prepare the NNM, and then MnO₂ and AC were loaded on the NNM substrate to prepared the NNM@MnO₂ and NNM@AC electrodes. The micro-morphology and dimensional change of the electrode during the preparation process are characterized by SEM. The PI fiber prepared by electrospinning is shown in Fig. 2a. The nanofibers have a diameter from 300 to 1000 nm and are bridged into a 3D skeleton with a porous structure. At the same time, these fiber bundles exhibit a relatively smooth surface. After magnetron sputtering a layer of Ni on the surface (Fig. 2b), the surface morphology was found to be rougher. SEM image (Fig. 2c) after electrochemical deposition of a layer of Ni shows that the fibers become thicker, and the diameter of the thinnest fiber bundle reaches more than 800 nm. At this time, a hierarchical structure of Ni-coated nanofibers was formed. The surface is also rougher than the original PI nanofibers, which increases the active site of the supercapacitor's active material to a certain extent. Fig. 2d shows the morphology after the deposition of MnO₂. MnO₂ forms spore-like nanoparticles, evenly covering the surface of NNM fibers, showing an attractive uniformly dispersed micro-morphology.



Fig.2 SEM figures of (a) electrospun PI fibers, fibers after (b) magnetron sputtering and (c) electrodeposition of Ni and (d) electrodeposition of MnO_2 .

After 2 minutes of electrochemical deposition, 0.5 mg/cm² MnO₂ was loaded onto the NNM skeleton. The CV characterization of the NNM@MnO₂ electrode at different sweep speeds are shown in Fig. 3a. The capacity of NNM@MnO₂ can be calculated to be 314.9, 279.1, 254.6, 233.1, 207.5, 187.75, 165.2 F/g at 2, 5, 10, 20, 50, 100, 200 mV/s from the CV curves,. It can be found that the NNM@MnO2 electrode exhibits standard capacitive electrode behavior. As the sweep speed increases from 2 mV/s to 200 mV/s, all of the CV curves show similar rectangles shape, indicating that the electrode has no obvious polarization and also good rate performance. The Ni deposited on the surface of the PI nanofiber increased the electrical conductivity, which ensures a fast electron transmission speed on the skeleton. The internal pore structure of the 3D skeleton allows the electrolyte to penetrate inside, and provides a large number of ion transport channels, thereby ensuring a fast ion transport. These factors can reduce the polarization and improve rate performance. The GCD curves of the NNM @MnO2 electrode at different current densities are shown in Fig. 3b. They maintain a very good linear shape, and the charge-



Fig.3 (a) CV characterization of the NNM@MnO₂ electrode at various scan rate, (b) GCD characterization of the NNM@MnO₂ electrode from 2 mV/s to 200 mV/s, (c) EIS characterization for the NNM@MnO₂ electrode from 100 kHz to 0.01 Hz and the inset is a magnification view in the high frequency range, (d) cycling stability of the NNM@MnO₂ electrode at 50 mV/s.

discharge process maintains a good symmetry. There is no obvious "voltage drop (IR) ", which means that the electrode material has a good charge and discharge reversibility and good rate performance. The NNM framework provides a large number of nanopores, high ionic conductivity, and high stability, all of which promote the improvement of the electrochemical performance of MnO₂ electrode materials.

EIS data was tested to analyze the electrical conductivity performance of the NNM@MnO₂ electrode. By fitting the results, it is shown that the ohmic resistance of NNM@MnO₂ is 2.959, which confirms that the composite electrode has good conductivity, and the charge transfer resistance is fitted to be 0.544, which confirms that the electrode has a very fast ion transmission. Such a small resistance can verify the origin of the excellent rate performance of the NNM@MnO₂ electrode. We conducted a long-cycle performance test at 50 mV/s to characterize the cycling stability of the NNM@MnO2 electrode. It can be found that the NNM@MnO₂ electrode is stably cycled, and it can still maintain 87.4% capacitance retention after 5000 cycles, which could be attributed to the good mechanical strength and flexibility of the NNM, and the even distribution of the MnO₂ on the surface-mentalized nanofibers, just as Fig. 2d shows.



Fig.4 (a) CV and (b) GCD characterizations of NNM@MnO₂//NNM@AC asymmetric supercapacitors, (c) CV curves when the supercapacitor is bent 0° or 180°, (d) cycle stability of NNM@MnO₂//NNM@AC at 50 mV/s.

To confirm the application value of the NNM@MnO₂ electrode, the NNM@MnO₂//NNM@AC asymmetric supercapacitor was assembled. The potential window of the entire asymmetric supercapacitor in the aqueous Na₂SO₄ electrolyte is 0-1.6 V. The CV test results of NNM@MnO₂//NNM@AC are shown in Fig.4a. Based on this result, the energy density was calculated to be 17.6 μ Wh/cm² while the power density is 2.0 mW/cm². In the process of increasing the sweep speed, the CV curves could maintain the shape, so it was confirmed that the device has good rate performance. The constant current charge-discharge curve is shown in Fig. 4b. This curve shows a shape close to a triangle, which proves that the charge-discharge process is very reversible.

In order to further evaluate the flexibility of NNM@MnO₂//NNM@AC asymmetric supercapacitor, we characterized the CV under the condition of bending. Fig. 4c shows the CV test results before and after bending, it can

be seen that the curves are almost consistent after bending 180°, thus confirming the excellent flexibility of NNM applied to the device. Characterizing the cycling performance of the NNM@MnO₂//NNM@AC asymmetric supercapacitor, it can be found that the capacity still maintained 67.2% of the origin after 3,000 cycles. Overall, the device maintains excellent flexibility while still exhibiting good cycle stability.

IV. CONCLUSIONS

In summary, we proposed a method for preparing a flexible supercapacitor skeleton substrate. The preparation processes of the substrate includes electrospinning, magnetron sputtering, and electrochemical deposition methods, which are simple and easy for industrial large scale production. After depositing MnO2 on the NNM substrate, the composite NNM@MnO2 electrode exhibited a high capacitance of 207.5 F/g at a sweep speed of 50 mV/s. The specific capacity has 87.4% capacity retention after 5000 cycles. With AC as the negative electrode, the NNM@MnO2//NNM@AC prepared asymmetric supercapacitor can show good flexibility. The superiority of these properties is mainly attributed to the following aspects: 1. The PI fiber has very good flexibility, 2. The 3D porous structure of the substrate provides a large number of ions transportation channels, 3. The NNM skeleton has very good electrical conductivity, resulting in good rate performance. The flexible supercapacitor device has good flexibility, excellent electrochemical performance, indicating that it has a very broad application prospect in the field of wearable portable electronic devices.

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