NiCo oxyfluoride non-woven cloth with ultra-high area capatitance for wearable supercapacitors

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Abstract-Supercapacitors, which serve as a kind of novel energy storage devices, are proven a promising solution for developing miniaturized, flexible, wearable electronics. Lightweight thin film electrodes that can be implemented is a potential developing orientation. Nevertheless, insufficient device energy density impedes its practical applications. To elevate device energy density, complicated assembly of nanostructured two-dimensional electrodes is a useful technique but results in high cost. Herein, we report a magnetic-assisted technology to fabricate tailorable, tractable, and flexible NiCo oxyfluoride non-woven cloth (NOC) for cathode, which can reveal superior electrochemical performance and excellent mechanical flexibility. A superb high areal capacitance up to 3.07 F cm⁻² and no significant capacitance decay after 5000 cycles reveal the great potential in practical applications of the NOC electrodes.

Keywords—NiCo oxyfluoride; three dimensional frame; supercapacitors

I. INTRODUCTION

Supercapacitors have been regarded as a type of promising energy storage devices with intriguing characteristics, which have accelerated the development of portable electronics. [1, 2] To better investigate the possibility of this uprising technology, tremendous contributions are made to these uprising energy storage devices. [3, 4] Basically, their electrochemical performance is partially subjected to the inherent features of electrodes and partially to the designed structures of materials. Therefore, increasing the specific surface area to enhance active sites and interface engineering are two common methods to elevate the utilization of the entire electrodes for better electrochemical performance, especially for planar film electrodes. [5, 6] In order to further improve electrochemical performance of planar electrodes, developing structural electrodes has been regarded as an efficient solution. [7-9] Herein, a bottom-up strategy is adopted while the thickness during fabricating structural electrodes is controllable via a two-step method assisting by magnetic field. Additionally, by virtue of nickel-cobalt core reduction, these linear structure exhibits excellent conductivity.

Transition metal oxyfluorides which comprise mixed anions with close ionic radii exhibit particular characteristics due to substitution between O²⁻ and F⁻. According to previous studies, exchange between these elements has a great impact on elevating electrical conductivity thus leading to unexpected excellent electrochemical performance. [10] Primarily, transition metal oxyfluorides are mainly applied in lithium batteries as potential cathode materials which however have only been investigated as electrodes in supercapacitors once to our knowledge. [11] To further understand these types of composites, we report a practicable technology hereto fabricate a three-dimensional and conductive NiCo oxyfluorides non-woven cloth electrode (NOC), consisting nickel-cobalt nanowire coated with NiCo oxyfluorides using a bottom-up strategy. Impressively, NOC electrodes with tunable characteristic structure and thickness exhibit excellent performance in supercapacitors, which can rival the majority of the-state-of-the-art metal-oxyfluoridesbased supercapacitors, holding great potential in future applications. [12]



Figure. 1. Illustration figure for fabricating method of NOC.

II. EXPERIMENTAL

A. Synthesis of NiCo non-woven cloth and fabrication of NOC electrode

NiCo non-woven cloth was prepared by one-step magnetic-field-assisted method (Fig. 1). [13] Solution A containing H2PtCl6·6H2O (0.0039 g), Na3C6H5O7·2H2O (6.617 g), NiCl₂ 6H₂O (7.133 g), CoCl₂ 6H₂O (2.377 g) with 100 mL deionized water and solution B with 5 wt% N₂H₄·H₂O in 100 mL deionized water were premixed respectively. Specific pH value (12.5) was adjusted for solution A and B for optimized synthesis. Next, both solution A and B were preheated to 60°C prior to the magnetic-assisted reactions. A one-step synthesis process was carried out by adding solution A and solution B together under a tunable magnetic field produced by Helmholtz coil (LITIAN, HCT-600) at 60°C for 5 hours. The reacting solution was placed in the middle of Helmholtz coil to ensure uniform magnetic field. Finally, the as-synthesized NiCo non-woven cloth was obtained for following treatments.

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The NOC electrodes were fabricated by immersing NiCo non-woven cloth in ethylene glycol (50 mL) with NH₄F (0.37 g) and deionized water (3.6 mL). Subsequently, anodic oxidation treatments was performed with a constant voltage of 20 V for 10 min. The NOC electrodes were then obtained. What was worth mentioning, the thickness of the NOC electrodes depended on the container during the synthesis of NiCo non-woven cloth. The optimized size of NOC (φ 12mm *50 um) electrodes was used for electrochemical measurements.

B. Fabrication of activated carbon@Ni foam (ACN) and cell of aqueous supercapacitor

The premixed slurry containing Super P65, acetylene black and PVDF (7:2:1 in mass ratio) was stirring in NMP overnight. Subsequently, screen printing was performed via a scraper of consistent height (25 um) at Ni foam with the prepared slurry. Activated carbon@Ni foam was cut into optimized pieces for single electrode (φ 12 mm) and cell (30*30 mm²) measurements after drying process at 60°C. For full cell assembly, ACN and NOC electrodes with similar capacitance were picked. Then, the NOC electrode was carefully placed in the middle of anode for optimized electronic and ionic transport. By integrating a 100 um thick commercial separator soaked with 1M KOH aqueous solution in between anode and cathode electrodes, the as-assembled cells were used for performance measurements.

C. Materials characterizations and electrodes electrochemical measurements.

Scanning electron microscopy (SEM) was applied for detailed understanding of the morphologies of NOC. To better study the structural information of materials we synthesized, X-ray diffraction (XRD) was performed all the way through 5 ° to 90 °. An automated adsorption device (Micromeritics) was used for acquiring and evaluating the BET results of NOC.

Electrochemical station (VMP3) was used for a series of unique electrochemical analytical techniques where Pt and calomel electrode serving as counter and reference electrodes were performed on the as-prepared samples to estimate the specific performance of the as-synthesized electrodes. The following equations were used to calculate specific value acquired from cyclic voltammetry (CV), and galvanostatic charging/discharging (GCD) curves, where the areal capacitance denoted as C_A , the volumetric capacitance denoted as C_V , the energy density denoted as E and the power density denoted as P.

$$C_{A} = \frac{I \cdot \Delta t}{\Delta U \cdot S} \tag{1}$$

$$C_{\rm V} = \frac{I \cdot \Delta t}{\Delta U \cdot V} \tag{2}$$

$$\mathbf{E} = \frac{\mathbf{C}_{\mathbf{V}} \cdot (\Delta \mathbf{U})^2}{2 \cdot 3600} \tag{3}$$

$$P = \frac{E}{\Delta t}$$
(4)

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{(C - 1)P}{V_m C P_0}$$
(5)

The above abbreviations were defined as the following descriptions, where Δt and ΔU were denoted as the discharging duration and the applied voltage window, S denoted as the total area, V denoted as whole volume, I denoted as the applied current, V_m denoted as monolayer adsorption saturation capacity of NOC respectively.

III. RESULTS AND DISCUSSION

Primarily, we introduced a unique technique to fabricate uniform nanowire-intercrossing NOC electrodes by anodic oxidation of the precursor NiCo non-woven cloth (Fig. 1). NiCo particles presented linear growth under the inducement of external magnetic field and shaped into non-woven structure till termination. No obvious shape deforming was found while the constant voltage treatment was performed on the NiCo non-woven cloth. Therefore, by adjusting the parameters of one-step magnetic-field-assisted synthesis of NiCo non-woven cloth, tunable, ordered, three dimensional, and free-standing NOC with great conductivity (Fig. 2a) was obtained via conformal transform.



Figure. 2. (a) Conductivity and intercrossing morphology of NOC. (b) High magnification SEM and EDS-mapping images of NOC (c) XRD patterns of pristine NiCo non-woven cloth and NOC. (Specific characteristic peak of Ni and Co were denoted by JCDPS card No.04-0850 and 15-0806.) (d) Adsorption isotherm pattern for BET analysis.

The formation of NiCo nanowire membrane was confirmed by X-ray diffraction analysis, as shown in Fig. 2c. NiCo non-woven cloth showed highly consistent signals of Ni and Co elements while NOC exhibited an unknown wide peak around low angles. Illustrated by Fig. 2a and Fig. 2b, nanowires with bumped surface (diameter about 100 nm) can be clearly found intercrossed with each other with short-range order structure. In addition, the EDS-mapping indicated uniform distribution of O, F elements and the intercalation of F⁻ into NOC. BET analysis was performed to evaluate specific surface area (SSA) in the view of SSA being concerned with more electroactive points. The adsorption isotherm pattern, as shown in Fig. 2d, indicated that the excellent SSA value of NOC was about 9.08 m² g⁻¹, which was significantly larger than commercial nickel foam $(0.1 \text{ m}^2 \text{ g}^{-1})$. In line with expectation, the specific C constant value defined by BET equations was 42.53, which can be ascribed to metal or oxides.

After anodic oxidation, in virtue of mismatched valence between O²⁻ and F⁻, vacancy defects generating during anodic oxidation may be advantageous to electronic transportation. The as-prepared NOC electrode with F⁻ in exchange of O²⁻ resulted in highly defective structure throughout the entire NOC. With the merit of large specific surface, intercrossing, and conductive, NOC electrodes exhibited excellent electrochemical performance during electrochemical analyses which implying NOC electrodes a competitive material to others. As shown in Fig. 3, the NOC electrode with 1M KOH as electrolyte solution showed superior areal capacitance, outstanding rate performance and excellent longevity. The shape of CV indicated a dominated oxidation peak at 0.39 V and a corresponding reduction peak without obvious secondary peak. A series of CV curves are displayed in Fig. 3. As depicted by the figure, no prominent distort or deform was found, implying excellent pseudocapacitive characteristic and high rate performance of NOC electrode. Meanwhile, slight peak shift occurred at higher scan rate, which was not only resulted from polarization, but also due the existence of bubbles generated on NOC at comparable high potential, thus impeding the interconnection of nanowire. The discharging curves exhibited a potential stage around at 0.3 V, consistent with the result of CV analysis (Fig. 3c). Based on the above result, the areal capacitance was estimated up to 3.07 F cm⁻². Additionally, the capacitance retention of NOC still maintained at 88.6% after 5000 cycles at 3 mV s⁻¹, indicating outstanding cycling stability.



Figure. 3. (a) CV curve of NOC electrode of single oxidation and reduction reaction. (b) CV curves of NOC electrodes. (c) Discharging curves of NOC electrodes. (d) Capacitance retention figure of NOC electrodes..

Activated carbon as a widely-used anode materials was chosen for relative reliable cycling capability in alkaline electrolyte solution, in comparison with conductive organic polymer (such as PANI, PPy and iron-based anode material). Electrochemical analytical techniques were used to evaluate the performance of ACN. As shown in Fig. 4a, several different scan rates were picked for CV analysis to evaluate rate performance. Besides, the capacitance retention can be remained at about 95% when discharging ranging from 1 A cm⁻³ to 50 A cm⁻³ according to the GCD curves. All these analyses demonstrated together that could serve as an excellent anode while assembling with NOC.



Figure. 4. (a) CV curves of ACN electrodes.. (b) Discharging curves of ACN electrodes.

Electrochemical performance of the as-assembled devices was estimated by analyses of CV, GCD and EIS measurements. The NOC-ACN cell exhibited a slight deform, as shown in Fig. 5a, indicating acceptable rate performance and superb energy density up to 12.62 mWh cm⁻³ at power density about 31.39 mW cm⁻³, according to the discharging curve (Fig. 5b) at a current density of 0.1 A cm⁻³. Attributed by the conductive, intertwined, and three-dimensional structure as well as abundant electrochemical active sites, the NOC-ACN cell displayed a slight decrement of 8.8% capacitance loss at a current density of 3.2 A cm⁻³, comparing with that at a current density of 0.1 A cm⁻³. After 5000 cycles, the capacitance retention was only about 69.2% (Fig. 5d), which was mainly due to the improper combination of electrodes. While more efforts should be focused on more suitable anode materials, NOC maybe an attracting choice as assembling for future wearable device. In this end, the Nyquist plot, as shown in Fig. 5c, was performed to better understand the interface of as-synthesized electrodes. The extremely low charge transfer resistance (R_{ct}) indicated the good contact between nickel-cobalt conductive core and active materials. Furthermore, the EIS analysis in low frequency represented fast ion mobility in electrolyte. The superior performance of NOC can be ascribed to following two aspects: 1) NOC with tunable, intercrossing, and conductive structure could easily be integrated in any other types of wearable device, owing to its outstanding flexibility and workability. 2) The F⁻ in exchange of O²⁻ resulted in more active surface areas during repeated charging and discharging cycles, especially in a form of nanowire network with defective surface.



Figure. 5. (a) CV curves of NOC-ACN cells. (b) Discharging curves of NOC-ACN cells. (c) Nyquist plot of the EIS for NOC-ACN cells. (Inset: magnified plot) (d) Cycling stability of NOC-ACN cells.

IV. CONCLUSION

Primarily, we successfully fabricated NiCo non-woven cloth as precursor of NOC electrode with the assistance of magnetic field. Owing to the merit of tunable structure, controllable thickness and excellent conductivity, which resulting from designed synthesis technique and metallic core, the NOC electrodes exhibited the superb high areal capacitance of up to 3.07 F cm⁻² and the superb volumetric energy density up to 12.62 mWh cm⁻³, by means of calculation, the corresponding power density up to 31.39 mW cm⁻³ was obtained. Therefore, with the concept of structural intercrossing network and feasibility of tunable, conductive NOC fabrication technique and method of ionic exchange integrated together, it may open up new possibilities for future high-performance wearable devices.

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