Research Article

Manganese Oxide on Carbon Fabric for Flexible Supercapacitors

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We report the fabrication of uniform large-area manganese oxide (MnO_2) nanosheets on carbon fabric which oxidized using O_2 plasma treatment (MnO_2/O_2 -carbon fabric) via electrodeposition process and their implementation as supercapacitor electrodes. Electrochemical measurements demonstrated that MnO_2/O_2 -carbon fabric exhibited capacitance as high as 275 F/g at a scan rate of 5 mV/s; in addition, it showed an excellent cycling performance (less than 20% capacitance loss after 10,000 cycles). All the results suggest that MnO_2/O_2 -carbon fabric is a promising electrode material which has great potential for application on flexible supercapacitors.

1. Introduction

With the rapid development of economy, the global energy consumption has been increasing for decades. As a result, the traditional fossil energy faces serious shortages. Green renewable energy such as solar cells and wind power generation set is desired. However, most of the new energy sources are intermittent and unsustainable, which hinder their application greatly [1, 2]. The energy supply gap deriving from the discontinuous characteristics of the renewable sources can be filled by coupling them with energy storage devices, such as supercapacitors (SCs) and batteries, which are able to store energy and deliver it to power the electronics [3–5].

SCs have drawn great attention in addressing the emerging energy demands due to the advantages of high power density, fast charge/discharge rates, and long cycle life [6–8]. Generally, SCs could be categorized into two types according to the charge storage mechanisms: electrochemical double layer capacitors (EDLCs) [9, 10] and pseudocapacitors (PSCs) [11–13]. EDLCs attract charges on the electrode-electrolyte interface of electrode materials electrostatically; meanwhile PSCs store energy via fast redox reaction on/near electrode surface [5, 14, 15]. Each of the two types of SCs has advantages and disadvantages, respectively. EDLCs use carbon materials such as carbon nanotubes (CNTs), graphene, carbon

nanofibers (CFs), and carbon onion as electrode materials, while PSCs employ transition metal oxides or conducting polymers such as manganese oxide (MnO_2), molybdenum trioxide (MoO_3), and polyaniline as electrode materials. Carbon materials usually hold higher physical and chemical stability, better electrical conductivity, and higher specific surface than those materials for PSCs, resulting in higher rate capability and longer durability than the latter. However, the theoretical capacitance of carbon materials is much lower than that for transition metal oxides, leading to the fact that most specific capacitance of carbon-based EDLCs are less than 150 F/g [3, 16–18]. On the contrary, PSCs exhibit higher capacitance and energy density through Faradic reaction, but suffered by the poor electrical conductivity [12, 19]. In this regard, if we can combine both the advantages of the two types of SCs and solve the shortcomings, then the SCs with enhanced electrochemical properties could be expected.

MnO_2 is one of the most attractive pseudocapacitive materials for the superior theoretical capacitance (1370 F/g), low cost, and abundance. Nevertheless, it suffered from the poor electric conductivity (10^{-5} – 10^{-6} S/cm), leading to the fact that the practice capacitance is much lower than the theoretical value [20, 21]. Growth of pseudocapacitive materials on well conductive carbon substrates not only can facilitate the diffusion of electrolyte ions but also can improve the transport of electrons, thus enhancing the electrochemical

FIGURE 1: Schematic of the fabrication procedure for MnO_2 -carbon composites.

properties [22, 23]. Furthermore, the hybrid structures may broaden their applications in energy storage device [24].

Herein, different surface treatments were employed to carbon fabric for assessing the influence of different treatments on the surface chemical states. We choose carbon fabric as substrates here for its low cost, good electrical conductivity, excellent chemical stability, and the flexible nature. Characterizations showed that the oxidic carbon fabric substrate is more suitable for electrodeposition of MnO_2 , for the reason of more oxygen containing functional groups which can act as nucleation points of MnO_2 . As a result, it exhibits a high specific capacitance (275 F/g) at a current density of 5 mV/s. In addition, the oxidic carbon fabric- MnO_2 showed excellent long-term cycle stability.

2. Experimental

2.1. Synthesis of MnO_2 /Carbon Fabric. The carbon fabric was oxidized or reduced using plasma technology. Firstly, carbon fabric was cut into the same size ($0.9 \times 1.8 \text{ cm}^2$). Then it was cleaned ultrasonically for 15 min by acetone, ethanol, and deionized water, respectively. After drying at 70°C , the carbon fabric was placed in plasma sample chamber for oxidation or reduction treatments. The treated carbon fabric was ready for next experiments.

A template-free electrodeposition method was introduced to fabricate MnO_2 /carbon fabric in a three-electrode cell. Carbon fabric, a graphite rod, and a saturated Ag/AgCl electrode were used as working electrode, counter electrode, and reference electrode, respectively. The solution containing 0.01 M manganese acetate (MnAc_2) and 0.02 M ammonium acetate (NH_4Ac) was used as electrolyte. The constant current and deposition time are 0.1 mA/cm^2 and 30 min, respectively.

2.2. Fabrication of SCs Electrodes. One piece of MnO_2 /carbon fabric was used as working electrode. The saturated Ag/AgCl electrode, a piece of pure Pt foil, and 1 M sodium sulfate (Na_2SO_4) aqueous solution were employed as reference electrode, counter electrode, and electrolyte, respectively.

2.3. Characterization. The morphology of MnO_2 /carbon fabric was analyzed using scanning electron microscopy (SEM, JSM-7100F). The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM) were performed on a JEOL-2010 HR transmission electron microscope to further investigate the internal structures and lattice fringes. The crystal structure of MnO_2 /carbon fabric was characterized by X-ray diffraction using the Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$) (XRD, D8-Advanced Bruker-AXS).

The electrochemical workstation (Chenhua, CHI 660D) was used to perform cyclic voltammetry (CV) and chronopotentiometry measurements. Autolab (PGSTAT302N) was used to measure the electrochemical impedance spectroscopy (EIS) with potential amplitude of 10 mV under the frequency ranging from 10 kHz to 100 mHz.

3. Results and Discussion

The fabrication procedure for the MnO_2 -carbon fabric composites is illustrated in Figure 1. Firstly, the carbon fabric cut in $0.9 \times 1.8 \text{ cm}^2$ is washed by deionized water, acetone, and ethanol, respectively. After drying, the carbon fabric was reduced or oxidized by plasma to add redox active functional groups on carbon fabric. Finally, the efficient electrodeposition method was adopted to prepare MnO_2 -carbon fabric composites.

The morphology of the original carbon fabric and as-prepared MnO_2 /carbon fabric samples was characterized by SEM, as shown in Figure 2. Figure 2(a) clearly shows that there is no other substance on the carbon fiber surface except very small amount of impurities. After electrodeposition, all the carbon fibers were covered by a multitude of MnO_2 on their surface (Figures 2(b)–2(d)). However, from Figures 2(b) and 2(c), it can be observed clearly that both the electrodeposition samples based on the pristine carbon fabric (MnO_2 /carbon fabric) and the carbon fabric reduced under Ar atmosphere (MnO_2 /Ar-carbon fabric) covered by many flower-like MnO_2 on the surface which exhibit uneven surface characteristics, suggesting lower pseudocapacitive electrochemical performance. Meanwhile, there is lots of sheet

FIGURE 2: The SEM images of (a) the rare carbon fabric, (b) MnO_2 /carbon fabric, (c) MnO_2/Ar_2 -carbon fabric, and (d) MnO_2/O_2 -carbon fabric.

MnO_2 covering densely the carbon fabric fiber surface which oxidized under O_2 atmosphere (MnO_2/O_2 -carbon fabric). The uniform surface morphology implies that it may have good electrochemical performance. Hence, we will further investigate the internal structure and electrochemical properties of MnO_2/O_2 -carbon fabric.

TEM was introduced to further investigate the morphology of MnO_2/O_2 -carbon fabric, as shown in Figure 3. According to the low resolution TEM image (Figure 3(a)), the electrodeposited MnO_2 is a sheet shape with a nanoscale thickness. HRTEM image (Figure 3(b)) shows the interplanar spacings for the two perpendicular directions to be ~ 0.48 nm. This value corresponds to d_{101} of the tetragonal MnO_2 phase (JCPDS reference card number 18-0802).

XRD pattern was collected from the electrodeposited products for investigating the crystal phase, as shown in Figure 4. From the spectrum, there are six peaks located at $2\theta = 11.4^\circ, 21.4^\circ, 36.5^\circ, 37.7^\circ, 41.3^\circ, 54.9^\circ$, and 65.7° . Among them, the broad peak located at 21.4° not only corresponds to the amorphous carbon but also can be assigned to the reflection

of (101) of tetragonal MnO_2 . Meanwhile, the other five peaks can be well assigned to the tetragonal MnO_2 (JCPDS reference card number 18-0802), which is consistent well with the TEM observations. Hence, the products synthesized by electrodeposition procedure are tetragonal MnO_2 .

To study the electrochemical performances of MnO_2/O_2 -carbon fabric, cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) were conducted using a three-electrode configuration with Ag/AgCl as reference electrode and 1M Na_2SO_4 as electrolyte. The typical CV curves of MnO_2/O_2 -carbon fabric are displayed in Figure 5(a) with scan rates from 5 mV/s to 100 mV/s. From the curves, even the scan rate has been increased to 100 mV/s; the CV curves retain a symmetrical rectangular shape, which demonstrate that the MnO_2/O_2 -carbon fabric not only holds rapid capacitive response but also has good electronic conductivity. In addition, the GCD curves of MnO_2/O_2 -carbon fabric collected at various current densities (Figure 5(b)) remain of semisymmetric shape revealing reversible ion adsorption/reaction on the surface and good Coulombic efficiency. Moreover, the

FIGURE 3: (a) TEM image and (b) HRTEM image of MnO_2/O_2 -carbon fabric.

FIGURE 4: The XRD pattern of the electrodeposited products.

IR drop derived from the GCD curves of MnO_2/O_2 -carbon fabric is as low as 0.05 V at 2 A/g, suggesting the MnO_2/O_2 -carbon fabric has good electrical conductivity. Combined with the excellent electrical conductivity of the carbon fabric and high theory capacitance value of manganese MnO_2 , enhanced properties are expected.

The specific capacitance derived from the discharge curves measured at different current densities could be calculated according to the following equation [1]:

$$C_s = \frac{Q}{\Delta U \times m}, \quad (1)$$

where C_s is the mass specific capacitance of the MnO_2/O_2 -carbon fabric, Q is the average electric quantity, ΔU is the working voltage window of the active material, and m is the mass of the active material.

The specific capacitance of the MnO_2/O_2 -carbon fabric calculated from their CV curves with different scan rates was

summarized in Figure 5(c). From the specific capacitance change curve, the specific capacitance value decreases along with the increase of the scan rate. The highest specific capacitance for MnO_2/O_2 -carbon fabric can achieve 275 F/g at the scan rate of 5 mV/s. This value is higher than those recently reported for other MnO_2 electrodes [25–27]. The specific capacitance of MnO_2/O_2 -carbon fabric still remains more than 45% (120 F/g) comparable with that obtained at 5 mV/s when the scan rate increases to 200 mV/s. It is important to note that the specific capacitance contribution of the carbon fabric is rather small [28, 29]. Thus, the MnO_2/O_2 -carbon fabric has high rate capability which provides a benefit for the potential applications. The high rate capability could be attributed to the unique free-standing composite structure including good-electrical-conductivity carbon fibers and disordered nanosheets which not only makes electron transportation and ion diffusion convenient, but also facilitates the reaction of active species, so that a good rate capability was obtained.

Beside high specific capacitance, good cycling performance is also one of the most important characteristics for high-performance supercapacitors [24]. In present work, GCD cycling at a current density of 5 A/g was employed to evaluate the long-term stability of the MnO_2/O_2 -carbon fabric electrode. From Figure 5(d), it is observed clearly that the specific capacitance for MnO_2/O_2 -carbon fabric remains more than 70% of the initial capacitance over the first 5000 cycles. Meanwhile, the capacitance even slightly increases to about 80% of the initial capacitance after 10,000 cycles. The specific capacitance increase of the MnO_2/O_2 -carbon fabric could be assigned to the following reasons: after the beginning circulations, the intercalation and deintercalation of the active species had been reacted completely, leading to the increase of active points; hence the specific capacitance was enhanced. This outstanding long-term stability performance could be attributed to the good contact between MnO_2 nanosheets and carbon fibers. Furthermore, this cycling performance is higher than those recently reported results

FIGURE 5: (a) Cyclic voltammogram curves, (b) galvanostatic charge-discharge curves, (c) specific capacitance, and (d) cyclic performance of MnO_2/O_2 -carbon fabric, respectively.

for MnO_2 nanotube arrays [30], MnO_2 nanowires [31], and hierarchical tubular MnO_2 structures [32].

4. Conclusions

In summary, uniform large-area MnO_2 nanosheets were successfully fabricated on flexible carbon fabric through a simple

electrodeposition method. The as-electrodeposited MnO_2/O_2 -carbon fabric was implemented as supercapacitor electrodes and shows outstanding electrochemical performance such as high specific capacitance and good cyclic stability. These results suggest that MnO_2/O_2 -carbon fabric is a promising electrode material which has great potential for application in flexible supercapacitors.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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