Mn_2O_3/ErGO Nanocomposites for Supercapacitor Electrodes

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Abstract In this report, we describe a simple two-step electrodeposition method to synthesis Mn_2O_3/electrochemically reduced graphene oxide (ErGO) nanocomposites on the surface of Ni foam (NF) and used as the electrode of supercapacitors (SCs). The scanning electron microscope (SEM), characterization had shown that three-dimensional (3D) Mn_2O_3 nanoflakes were uniformly loaded on the ErGO/NF. The electrochemical experiments show that the introduction of ErGO improve the electrochemical performance of Mn_2O_3 greatly due to the large surface area and high conductivity of ErGO, which provide enough place for Mn_2O_3 and decrease the resistance. In addition, the 3D network of Mn_2O_3 also own high surface area and porous structure. In one word, the synergistic effect of the ErGO and 3D network of Mn_2O_3 made the electrode possesses high specific capacitance of 114.3 F g^{-1} at a current density of 1 A g^{-1}.

Introduction

With the development of the portable electronics and depletion of fossil fuels, energy storage and conversion device such as supercapacitors (SCs)[1-3], lithium-ion batteries (LIBs)[4] and fuel cells (FCs)[5] have received much attention. Among them, SCs, also known as ultracapacitors or electrochemical capacitors, are considered as promising candidates for energy storage which exhibit high power density, fast charge and discharge rates and long cycle life[6]. According to the storage mechanisms, SCs can be classified as electrochemical double-layer capacitors (EDLCs) and pseudocapacitors[7]. Electrode material is the key to the performance of SCs, therefore, great efforts have been devoted to the synthesis of advanced electrode materials with excellent electrochemical performance.

Transition metal oxides and hydroxides such as Co_3O_4[8], MnO_2[9], NiO[10] and $Ni(OH)_2$[11] are competitive materials for electrochemical energy storage. Manganese oxides, characterized by a low-cost material with abundant oxidation valence states and environmentally friendly nature, have attracted significant interest as a promising alternative electrode material for SCs. However, the low conductivity limit its wide application. For this reason, nanocomposite materials including carbon materials, transition metal oxides or hydroxides have attracted broad attention due to rich nanostructure, low cost and high electrochemical activity[12-14].

Graphene and its derivatives, as a kind of unique and attractive material, composed of atom-thick two-dimensional (2D) structure, has been extensively explored for applications in fabricating electronic and energy storage devices[15], sensors[16] and nanocomposites[17], owing to its superior properties such as fast ion diffusion, high electronic conductivity, large specific surface area and great mechanical strength[18]. Many methods have been used to prepare grapheme such as mechanical exfoliation, chemical vapor deposition and epitaxial growth. Reducing of graphene oxide (GO) by electrochemical technique is the most promising approach for producing graphene due to the low-cost and readily scalable to industrial levels[19].

Recently, considerable efforts have been devoted to fabricating graphene-based nanocomposites for high-performance SCs[20]. Wang. *et al.* demonstrated that MnO_2/graphene aerogels(GA) electrodes exhibited a high specific capacitance of 410 $F\Box g^{-1}$ at 2 $mV\Box s^{-1}$[21]. Tong's group reported a 3D MnO_2-graphene nanocomposites for SCs with high areal capacitance of 3.18 $F\ cm^{-2}$[22]. Based on the above considerations, we develop a simple two-step electrochemical deposition method to prepare Mn_2O_3/ErGO on NF. This material was used as the electrode for SCs and the electrochemical experiments show high performance in SC application.

Experimental

Preparation of Mn_2O_3/ErGO/NF electrodes. GO was synthesized from graphite powder by the modifed Hummers' method.[23] 20 mg GO was mixed with 20 mL PBS solution (pH 8.0) and ultrasonicated for 2 h to yield a stable GO suspension (1 mg mL^{-1}). Typically, the ErGO/NF electrode was fabricated by electrochemical reduction of GO suspension on a piece of NF under a constant potential of -1.2 V (vs.SCE) for 600s. After that, the observed ErGO/NF electrode was immersed in the 0.5 M sodium sulfate aqueous solution containing 0.1 M manganese acetate with a constant potential of -1.2V for 300 s, then wash the electrode with deionized water for several times and then dried at room temperature. The observed electrode was Mn_2O_3/ErGO/NF.

Results and discussion

Structure and morphology. The electrode morphology was characterized by SEM. Fig. 1 a-c clearly show the surface morphology of ErGO/NF. The 3D network shows in Fig. 1a was the typical framework of NF. The high magnificent SEM images in Fig. 1b and c shows obvious wrinkle structure, which suggests the existence of ErGO. The unique structure of ErGO can increase surface area and load much more active material, which result in the high specific capacitance. Fig. 1d show a 3D network with relatively rough surface, which indicate the successful deposition of Mn_2O_3 in the surface of ErGO/NF. Fig. 1e and f shows many nanoflakes are grown vertically, forming a three dimensional structure. The nanostructure of Mn_2O_3 can provide a high specific surface area and multi-pathway for charge transfer, which is foundation for a high specific capacitance and low electrode resistances.
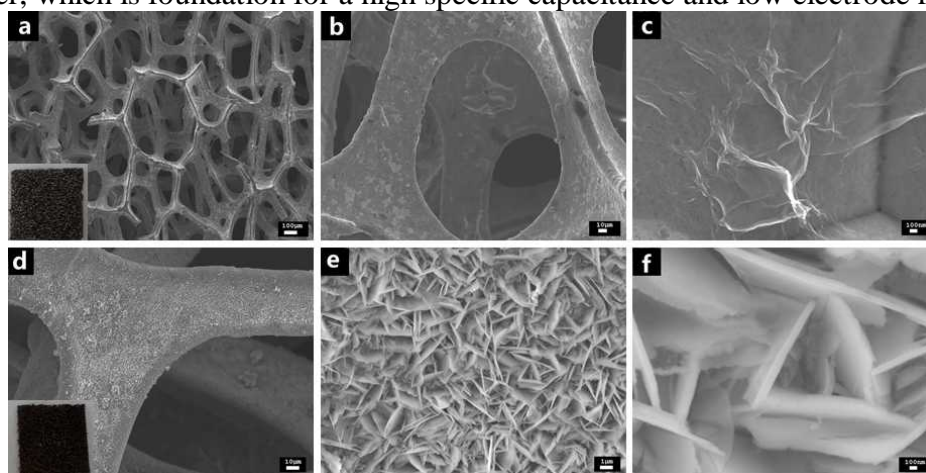

Figure 1 SEM images for ErGO (a-c) and Mn_2O_3/ErGO nanoflakes (d-f) on NF

The Raman spectra was recorded to study the structure change of GO before and after electrochemical reduction. As shown in Fig. 2, Both of the spectra of GO and ErGO display the existence of D and G bands located at about 1352 and 1585 cm^{-1}, respectively. The intensity ratio (I_D/I_G) of D and G bands is 0.97 in GO and increases to 1.06 in ErGO, demonstrating that the chemical reduction altered the structure of GO and introduced a large number of structural defects.
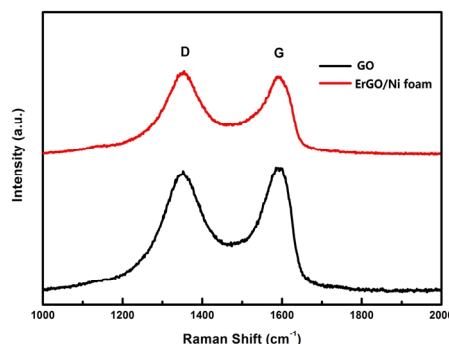
Figure 2 Raman spectra of GO, ErGO

EDS spectra in Fig. 3 (a) confirms the presence of the elements of manganese, oxygen, carbon and nickel in the deposited materials, whereas no other chemical elements. Fig. 3(b) is XRD pattern with a strong diffraction peak at 2θ values of 32.9˚ and a few relatively weak but obvious diffraction peaks at 35.9˚, 39.4˚, 54.3˚. Compared to the standard card (PDF# 41-1442), it confirmed that we got Mn_2O_3. The above characterization results show that Mn_2O_3/ERGO/NF was successfully obtained by two-step electrodeposition.
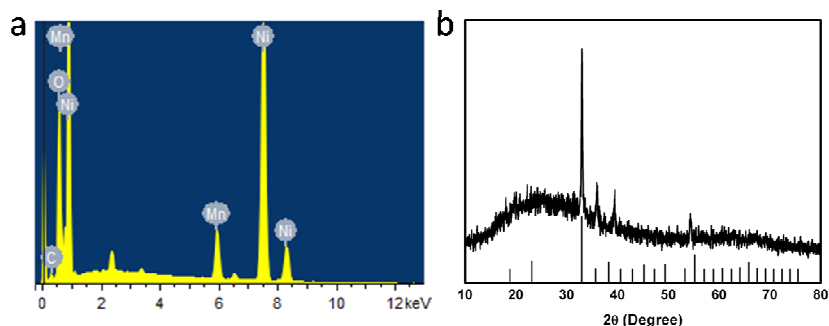

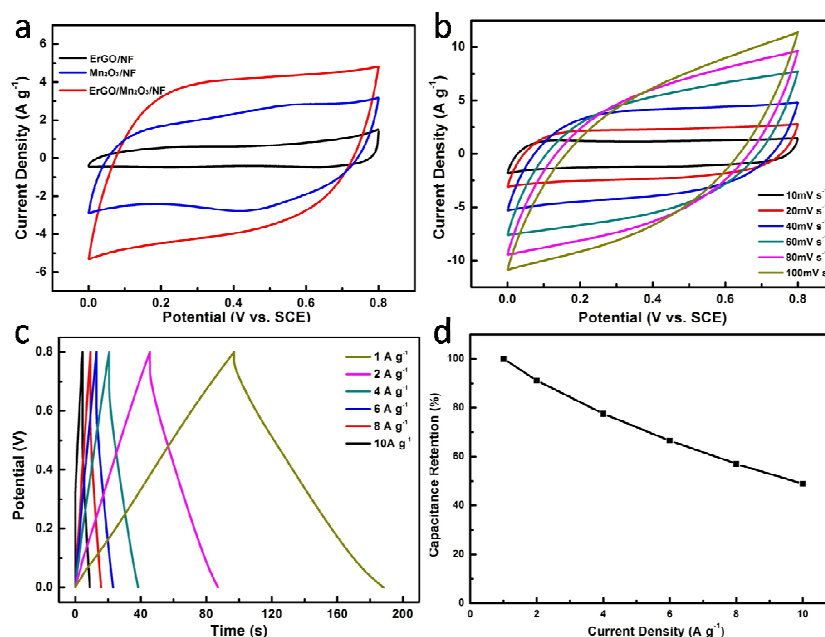Figure 3 (a)EDS spectra and (b) XRD pattern of Mn_2O_3/ErGO/NF electrode.

Figure 4 (a) Cyclic voltammograms of ErGO/NF, Mn_2O_3/NF and Mn_2O_3/ErGO/NF at a scan rate of 40 mV s^{-1}. Electrochemical properties of Mn_2O_3/ErGO/NF electrode: (b) cyclic voltammograms at different scan rates, (c) the galvanostatic charge-discharge curves at different current densities, and (d) specific capacitance derived from the discharge curves at different current densities.

Electrochemical capacitive properties for SC. Fig. 4(a) shows the CV curves of ErGO/NF, Mn_2O_3/NF and Mn_2O_3/ErGO/NF collected in 0.5 M Na_2SO_4 electrolyte in the potential range of 0~ 0.8 V at a scan rate of 10 mV s^{-1}. The nearly rectangle shape and no obvious reduction and oxidation peaks appear i indicating the ideal capacitive behavior of SCs. In addition, the close area of the Mn_2O_3/ErGO/NF is much higher than pristine ErGO/NF and Mn_2O_3/NF, which suggests the Mn_2O_3/ErGO/NF electrode has higher specific capacitance which due to the supporting of ErGO. The CV curves of Mn_2O_3/ErGO/NF at different scan rates were obtained in Fig. 4b. No obvious change was found in the curves shape with the increasing scan rate, indicating the high rate capability. The GCD curves were also tested at various current densities ranging from 1 to 10 A g^{-1}. As shown in Fig. 4c, nearly symmetrical shape of the GCD curves in the total range of potential indicate good capactive and reversibility of the electrode. The specific capacitance also can be calculated from the GCD curves according to the following equation:

$$C = (I \cdot \Delta t)/(m \cdot \Delta V) \tag{1}$$

where C (F g^{-1}) was specific capacitance, I (mA) represented discharge current, and m (mg), ΔV(V), and Δt (s) designated mass of active materials, potential drop during discharge, and total discharge time, respectively.

Based on the above equation, the specific capacitance of the Mn_2O_3/ErGO/NF electrode is calculated to be about 114.3 F g^{-1} at 1 A g^{-1}. This demonstrates that the obtained Mn_2O_3/ErGO/NF electrode has good capacitance characteristics. Meanwhile, the specific capacitance values of the electrode were measured to be 93.67, 80.2, 68.89, 60.45 and 55.9 F g^{-1} at 2, 4, 6, 8 and 10 A g^{-1}, respectively, 48.9% of capacitance is maintained (shown in Fig. 4d).
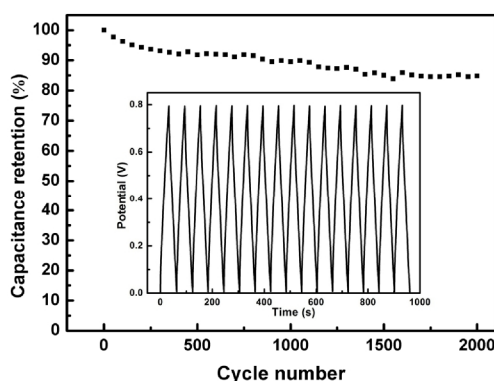

Figure 5 Cycling stability curve of the ErGO/Mn_2O_3/NF electrode, the inset: continuous 1000s charge-discharge curves at 2 A g^{-1}

It is very important for electrode materials to have good cycling stability. As shown in Fig. 5, the 3D Mn_2O_3/ErGO/NF electrode retained more than 84.8% of its initial capacitance after 2000 cycles at 2 A g^{-1}. The inset of Fig. 5 shows consecutive charge and discharge curves for 1000 s at 2 A g^{-1}. Each curve has the same shape, explaining good repeatability of the electrode material. These results demonstrates that the Mn_2O_3/ErGO/NF electrode is a potential candidate for SCs.

Conclusions

In summary, we adopted a facile two-step electrodeposition to prepare Mn_2O_3/ErGO/NF electrode. The as-prepared electrode delivers a specific capacitance of 114.3 F g^{-1} at 1 A g^{-1}. ErGO is not only provide enough place for Mn_2O_3, but also increase the conductivity of electrode, which is the key to high electrochemical performance. In addition, the structure of Mn_2O_3 provide multi-path for ions and electronics, which promote the fast rate of ions diffusion and electronic transfer. Our work confirms that the Mn_2O_3/ErGO/NF electrode has potential use as a high-performance SC.

Acknowledgements

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