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Microwave-assisted synthesis of functionalized graphene on Ni foam as electrodes for supercapacitor application

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ABSTRACT

The electrodes of supercapacitors were prepared via a simple and convenient strategy by microwave-assisted synthesis of functionalized graphene on Ni foam (FG-Ni foam) in ambient condition. The functionalized graphene on Ni foam was directly used as electrode for electrochemical double layer capacitance without any conductive agents and polymer binders, such as acetylene black and polyterafluoroethylene. The direct contact between FG and the foam current collector without any polymer binder helps to decrease the resistance of the FG-Ni foam electrode and improve the cycle life of the supercapacitor based on the FG-Ni foam electrodes. FG-Ni foam exhibits good electrochemical performance with a maximum specific capacitance of 265 F g^{-1} at the charge/discharge current density of 1 A g^{-1} with 5 M NaOH as electrolyte. After 10,000 cycling GCD tests, a high level retaining specific capacitance of 261 F g^{-1} was obtained which still retained 97.7% of the initial capacity and the charge/discharge efficiency was approximate to 99.9%.

1. Introduction

Nowadays, the consumption of fossil fuels and low efficient use of renewable energy have led to the accelerating development of energy conversion/storage systems which can satisfy with the energy demands [1,2]. Supercapacitors based on electrochemical double layer capacitance (EDLC), as one of the most promising electrochemical energy conversion/storage systems, have attracted increasing attention due to their higher power density, longer cycle life and higher energy density compared with electrostatic and electrolytic capacitors. The energy conversion/storage capacity of EDLC depends on the electrostatic forces based on the electrical double layers which form at the interface between electrode and electrolyte [3]. Since the electrode materials play an important role in the performance of supercapacitor, greater efforts have been spent on the preparation of electrode materials with high specific capacitance and long cycle life. Carbon-based material represents a very promising material for supercapacitor application owing to its unique chemical stability, good conductivity, high specific surface area and rich sources. The carbon-based materials for electrochemical double layer capacitor mainly include active carbon [4–6], carbon fiber [7,8], glassy carbon [9], graphite [10,11], carbon black [12], carbon aerogels [13], carbon nanotubes [14] and graphene [15–18]. Due to its distinctive electronic, thermal, optical and mechanical properties, graphene has gained tremendous attention. Graphene is a two-dimensional monolayer of carbon atoms packed into a honeycomb lattice which was discovered by Geim and Novoselov in 2004 [19]. Graphene has a very special electronic structure due to the π and π^* bands touch in single point at the Fermi energy at the corner of the Brillouin zone and close to the Dirac point, which gives rise to its excellent electronic properties [20,21]. At room temperature, the carrier mobility and thermal conductivity of graphene are up to 200,000 $cm^2\ V^{-1}\ S^{-1}$ and 5300 $W\ m^{-1}\ K^{-1}$ [22,23] respectively, which are of great benefit to reduce the internal resistance and improve the thermal performance of supercapacitor. In addition, the theoretical specific surface area of single-layer graphene is as high as 2600 $m^2\ g^{-1}$ [24]. The specific capacitance of single-layer graphene measured by CV was 21 $\mu F\ cm^{-2}$, thus the theoretical specific capacitance of graphene electrode in EDLC is up to 550 F g^{-1} [25]. Therefore, graphene shows widely potential application in supercapacitors.

Up to now, many studies have been reported on the synthesis of graphene and its application in supercapacitors. Stoller et al. [15] had pioneered a new carbon material called chemically modified graphene and demonstrated that the specific capacitance of this ultracapacitor cell are 135 and 99 F g^{-1} in aqueous and organic electrolytes at 20 mV s^{-1}, respectively. Yuyan Shao et al. [16] had synthesized graphene via electrochemical reduction of graphene oxide (ER-G). The maximum specific capacitance of ER-G measured by CV at the scan rate of 20 mV s^{-1} and by GCD at the current density

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of 5 A g^{-1} in 0.1 M Na_2SO_4 were 164.8 and 150.4 F g^{-1}, respectively. Ye et al. [17] had prepared thermally exfoliated graphite oxide at a low temperature and ambient pressure. With KOH as the electrolyte, the GCD measurements showed a specific capacitance of 315 F g^{-1} at the current density of 100 mA g^{-1}. After 1000 cycles, the specific capacitance decreased from 315 to 258 F g^{-1}. Zhu et al. [18] had reported a facile and efficient method to achieve the exfoliation and reduction of graphite oxide by treating graphite oxide powers in a commercial microwave oven, and obtained reduced graphene oxide (RGO) within 1 min in ambient condition. The specific capacitance value of this graphene-based supercapacitor was as high as 191 F g^{-1} at a constant current of 150 mA g^{-1} in 5 M KOH electrolyte.

Above all graphene-based supercapacitor electrodes were prepared by mixing graphene with conductive agents (acetylene black) and polymer binders (polyterafluoroethylene) uniformly at an appropriate weight ratio and then the mixture was spread on a current collector such as Ni foam or copper foil. However, the as-prepared supercapacitors may suffer from low rate capability and poor stability because the polymer binders are usually insulating which hinder the fast electron transport required for high charge/discharge rates and become invalid after long cycles.

Recently, the combination of graphene with current collector directly without any conductive agents or polymer binders had been proved to be an effective way to improve the electrochemical performance. Chen et al. [26] had successfully synthesized a three-dimensional flexible and conductive interconnected graphene network grown on Ni foam by chemical vapor deposition. The three-dimensional foam-like graphene macrostructures, called graphene foams, can be used as the fast transport channel of charge carriers for high electrical conductivity. Y.J. Mai, J.P. Tu, et al. [27] had also reported a direct synthesis of graphene on Ni foam by CVD method. The underlying 3D grapheme network afforded an electrical contact for fast charge transfer from active material to current collectors and can be served as a platform to construct graphene/metal oxide composites for surpercapacitor application. The obtained composites showed a specific capacitance of 745 F g^{-1} at a discharge current density of 1.4 A g^{-1}, and there was no obvious capacitance drop over 2000 cycles.

In this paper, we report a simple and convenient method to prepare supercapacitor electrode by microwave-assisted synthesis of functional graphene on Ni foam (FG-Ni foam) without any conductive agents and polymer binders, different from the conventional preparation methods of electrodes. The supercapacitors based on the as-prepared FG-Ni foam electrodes showed high specific capacitance, long cycle life at high current density and excellent stability of charge/discharge efficient.

2. Experimental

2.1. Preparation of FG-Ni foam

Graphite oxide was prepared by a modified Hummers method. In a typical preparation procedure, 92 mL of concentrated H_2SO_4 solution was added into a 1000 mL three-neck flask which was placed in a low temperature thermostat bath of 3 °C. Then a mixture of graphite power (4 g) and $NaNO_3$ (2 g) was added into the solution under continuous stirring. Potassium permanganate (12 g) was then slowly added into the above solution and kept in cooling condition for 2 h. Afterwards, the temperature of the thermostat bath was raised from 3 °C to 35 °C, and the dark green mixed solution was stirred for another 2 h. Distilled water (184 mL) was gradually added into the dark brown solution, and the mixture was heated to 75 °C. After stirring for 10 min, a suitable amount of 5% H_2O_2 was slowly added into the mixture to remove the unreacted potassium permanganate. The color of the mixed solution turned from dark brown into brilliant yellow. The reaction equation can be expressed as follows:

$$5KMnO_4 + 5H_2O_2 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 5O_2\uparrow + 8H_2O \quad (1)$$

The mixture was filtered and washed using 10% HCl until the sulfate ions could not be detected by $BaCl_2$. The graphite oxide in the state of colloid was kept at room temperature.

After pickling and alkaline cleaning, the Ni foam was soaked into the GO colloid for 0.5 h, and excess GO was scraped off the Ni foam with a copper slice. The GO-coated Ni foam was then put into a drying oven and dried at 30 °C for 2 h. By microwave irradiation of the dried GO-coated Ni foam in a microwave oven at 1000 W for 2 min in ambient condition, a silver black FG-Ni foam sample was obtained.

The schematic procedure for the preparation of FG-Ni foam is shown in Fig. 1. For comparison, the functional graphene (FG) was also prepared by reducing GO under the same condition.

2.2. Characterization of FG and FG-Ni foam

X-ray diffraction (XRD; DMAX-Ultima IV, Rigaku Corporation, Japan) and Fourier transform infrared (FTIR; Nicolet 380, Nicolet, USA) were employed to identify the FG-Ni foam crystal structure and the chemical bands of FG and GO samples. The molecular vibration mode and defect of FG were measured by Raman spectra (Renishaw 2000 Confocal Raman Microprobe; Renishaw Instruments, English) and the morphology and the chemical composition of samples were investigated by scanning electron microscopy (SEM; S3400 N, Hitachi, Japan) with an energy dispersive X-ray spectroscopy detector, field emission scanning electron microscopy (FE-SEM; Quanta 200F, FEI, Holand) and transmission electron microscopy (TEM; JEM-2010HR, Jeol, Japan).

2.3. Electrochemical measurements

The supercapacitor electrodes were prepared directly using the as-prepared FG-Ni foam without any conductive agents or polymer binders. The FG-Ni foam was sliced into a 16.2 mm diameter wafer and packed into button cell supercapacitors using 5 M NaOH aqueous solution as electrolyte. The electrochemical properties of packaged button cell were studied by cyclic voltammetry, galvanostatically charge/discharge measurements and AC impedance test. The Nyquist plots and CV curves were measured by an electrochemical work station (CHI660C; CH Instruments, Shanghai Chenhua Instrument Corporation, China) with potential from −0.2 to 0.8 V at the scan rate of 1, 5 and 10 mV s^{-1}, respectively. The cycle performance and the charge/discharge efficiency were tested by a LAND battery tester (CT2001A, Wuhan LAND Corporation, China) and the current densities of charge/discharge varied from 1 A g^{-1} to 2 A g^{-1}. Meanwhile, FG-pressed Ni foam (FGp-Ni foam) was prepared by mixing the FG with acetylene black and polytetrafluoroethlene at a weight ratio of 8:1:1, which was then pressed onto Ni foam to form the supercapacitor electrodes. The FGp-Ni foam was tested under the same condition as that of FG-Ni foam.

3. Results and discussion

The phase structure of the FG-Ni foam was characterized by XRD measurements as shown in Fig. 2. The peaks at 44.54°, 51.92° and 76.38° correspond to (1 1 1), (2 0 0) and (2 2 0) planes of face centered cubic (fcc) Ni, respectively [27]. However, the feature peak of GO centered at 10.82 ° completely disappears after microwave irradiation. A weak broad peak relating to FG appeared at around 26°,