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One-step fabrication of electrochemically reduced graphene oxide/nickel oxide composite for binder-free supercapacitors

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ABSTRACT

A three-dimensional (3D) graphene/Nickel oxide (ERGO/NiO) composite electrode have been fabricated directly on a Nickel foam substrate via a one-step electrochemical co-deposition in an aqueous solution containing Nickel nitrate and GO. By using this simple and one-step electrochemical deposition, it is possible to produce binder-free composite electrodes with improved electrochemical properties using a low-cost, facile and scalable technique. It is observed from FE-SEM images that graphene oxide sheets affect the electrodeposition of nickel oxide. The optimized ErGO/NiO electrode developed in this work exhibits high charge storage capacity with a specific capacitance of 1715.5 F g^{-1} at current density 2 A g^{-1} and hierarchical morphological structure which facilitates electrolyte diffusion to the electrode surface. A good cycling stability was observed for the modified electrodes in alkaline media. EIS measurements showed low values of internal resistance (R_s) and charge transfer resistance (R_{ct}) for the modified electrodes, indicating that the prepared nanocomposite is appropriate for supercapacitor applications in comparison to NiO/NF electrode.

Introduction

The increasing of energy consumption and growing concerns about environmental pollution and global warming have stimulated researches on energy storage and conversion from alternative energy sources. In this case, Supercapacitors; which are also known as ultra-capacitors or electrochemical capacitors, have attracted great attention in recent years as promising energy storage devices due to their high power density, rapid charging/discharging rates, long cycle life and low maintenance cost [1–4]. Generally, supercapacitors can be divided into electric double-layer capacitors (EDLCs) and pseudocapacitors based on their charge storage mechanisms. As EDLCs, involve electrochemical inactive materials with high surface area which used to store energy through charge accumulation at the electrode/electrolyte interface. EDLCs show ultrahigh power density and excellent cycle life; however, their specific capacitances and energy densities are usually restricted by the limited effective surface area of active materials. Pseudocapacitors on the other hand, are dominated by reversible and fast Faradaic reactions on the surface of electrode materials. Compared with EDLCs, pseudocapacitors exhibit better specific capacitances and higher

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energy densities, but usually suffer from poor electrical conductivity. Generally, the material components of supercapacitors can be classified into three major categories: (1) carbon materials such as activated carbon, carbon nanotubes, graphene and etc. [5–7], (2) conductive polymers, such as polyaniline and polypyrrole [8–10] and (3) transition metal oxides and hydroxides, such as RuO_2, NiO, MnO_2 and CuO [11–13].

Nanostructured transition metal oxides and hydroxides have attracted extensive attention in Electrochemical Capacitors (ECs) since they exhibit illustrious properties including high redox activity and capacity [11–13]. As an important family of metal oxides, cobalt and nickel oxide plays a significant role in ECs [14–18]. However, low electrical conductivity of these materials limits their application in ECs. In order to overcome this problem, synthesizing composites of them with different carbon based materials with high electrical conductivity is a significant strategy to improve their specific capacitance.

Among various carbon materials for energy storage devices, graphene is considered as the most promising electrode material [19]. Recently, graphene nanosheets have been attracted a great deal of attention due to their unique electronic, mechanical and thermal properties such as ultra-high electrical conductivity (10^3–10^4 S m^{-1}), specific surface area (theoretical value ~2630 m^2 g^{-1}) and good thermal conductivity (~5000 W m^{-1} K^{-1}) [20–22]. As a result, tremendous researches have been devoted to discovering interesting characteristics of graphene-based materials over the past few years. For this reason, various graphene composites with transition metal oxide or hydroxide have been fabricated to be used as electrode materials for supercapacitors [14–18].

In this regard, different routes have been used for the fabrication of graphene–metal oxides/hydroxide composite electrodes including chemical vapor deposition [23–25], chemical and hydrothermal precipitation [26,27], microwave assisted synthesis [28–30] and electrochemical deposition [7,31,32]. Among all the above mentioned methods, electrodeposition is a simple, rapid, green and low cost approach, which allows tailoring not only the metal oxide/hydroxide composition but also the porosity (pore size and morphology) of the final product to achieve optimized electrochemical behavior of the resulting electrodes. Moreover, through this method, the composite can be produced directly onto the current collector, avoiding the use of binders and additives that introduce additional resistances to the electrode [33].

Different electrochemical approaches including potentiostatic, galvanostatic, potentiodynamic and pulse methods can be used to deposit electroactive materials on the surface of the electrodes [34]. Among these various electrodeposition techniques, potentiodynamic route have been attracted extensive attention since it can lead to more controlled deposits compared to other methods due to the "discontinuous" deposition process associated with a break in the deposition conditions during each cycle [35,36].

One-step electrochemical co-deposition of graphene and metal oxide/hydroxides is of great importance due to the simplicity and time saving procedure. In this regard, Zhao et al., co-electrodeposited a MnO_2/graphene oxide coating on carbon paper using cyclic voltammetry and the composite used as electrode for SCs (Supercapacitors), which displayed increased electrochemical charge storage ability, attaining specific capacitances of 829 F g^{-1} at current density of 1 A g^{-1} [37]. More recently, García-Gómez and co-workers [38] electrodeposited CoO_x/graphene foams, using a one-step electrodeposition process on stainless steel substrate. The optimized ERGO/CoO_x developed in that work exhibits a specific capacitance of 608 F g^{-1} at a current density of 1 A g^{-1} and increased reversibility when compared to single CoO_x.

Herein, for the first time an ERGO/NiO composite was synthesized on nickel foam substrate by a one-step potentiodynamic procedure in the potential range of −0.5 to −1.5 V vs Ag/AgCl (3.5 M) in a solution containing 1 mg mL^{-1} GO and 10 mM nickel nitrate as electrolyte. In order to obtain the optimum condition for the electrochemical deposition, various scan rates between 50 and 200 mV s^{-1} were selected to deposit the composite material. On the other hand, to investigate the effect of GO nanosheets, NiO electrode was also prepared in the absence of GO in the electrolyte solution. The electrochemical results revealed that 3D nickel foam/ERGO/NiO architecture has superior electrochemical properties including high capacitance, good cycling stability and good rate capability performance.

Experimental

All chemicals were of analytical reagent grade purchased from Sigma Aldrich and used as received without any further purification. Also, all aqueous solutions were prepared with DI water (Millipore Water Purification, 18 MΩ).

Synthesis of graphene oxide

Graphene oxide (GO) nanosheets were synthesized by the modified Hummers method as reported by Marcano et al. [39]. In brief, concentrated H_2SO_4 was added to a mixture of graphite flakes and $NaNO_3$, and the mixture was cooled to 0 °C using an ice bath. $KMnO_4$ was added slowly in portions to keep the reaction temperature below 20 °C. The reaction was heated to 35 °C while stirred for 7 h. Additional $KMnO_4$ was added in one portion, and the reaction was stirred for 12 h at 35 °C. The reaction mixture was cooled to room temperature and poured onto ice containing 30% H_2O_2. Finally, the GO suspension was filtered until the pH of supernatant become neutral.

Synthesis of ERGO/nickel oxide nanocomposite

Graphene oxide with a concentration of 1 mg mL^{-1} was dispersed in DI water and then to this dispersion, 0.1454 g $Ni(NO_3)_2.6H_2O$ and $NaNO_3$ 0.1 M was added under magnetic stirring. This suspension was sonicated for 1 h and used as a supporting electrolyte for electrodeposition of graphene/nickel hydroxide composite.

Electrochemical experiments were performed by an Autolab PGSTAT 101 (Metrohm, Netherlands) in a three–electrode system with Nickel foam (1 cm × 1 cm), Pt foil (1 cm × 2 cm) and Ag/AgCl (KCl, 3.5 M) as working, counter and reference electrodes, respectively. Potentiodynamic route was used for