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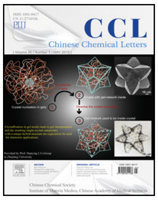

Original article

A facile preparation and electrochemical properties of nickel based compound–graphene sheet composites for supercapacitors

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ABSTRACT

Composites of a nickel based compound incorporated with graphene sheets (NiBC–GS) are prepared by a simple flocculation, using hydrazine hydrate as flocculant and reductant, from a homogeneous intermixture of nickel dichloride and graphene oxide dispersed in *N*,*N*-dimethylformamide. Morphology, microstructure and thermal stability of the obtained products were characterized by field-emission scanning electron microscopy, X-ray diffraction and thermal gravimetric analysis. Furthermore, the electrochemical properties of NiBC–GS, as electrode materials for supercapacitors, were studied by cyclic voltammetry and galvanostatic charge/discharge in 2 mol L^{-1} KOH solution. It was determined that for NiBC–GS annealed at 250 °C, a high specific capacitance of 2394 F g^{-1} was achieved at a current density of 1 A g^{-1}, with 78% of the value (*i.e.*, 1864 F g^{-1}) retained after 5000 times of repeated galvanostatic charge/discharge cycling. The high specific capacitance and available charge/discharge stability indicate the synthesized NiBC–GS250 composite is a good candidate as a novel electrode material for supercapacitors.

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1. Introduction

Supercapacitors are gaining increased attention owing to the diminishing supplies of fossil fuel and the rapid growing demand for renewable sources [1]. It is well known that the most frequently used materials for supercapacitors are mainly carbon-based materials [2–4], conducting polymers [5] and transition metal oxides [6,7]. Carbon-based materials have advantages with regard to their high specific surface area, high power density and excellent electric conductivity. However, carbon-based materials are known to have low specific capacitance and are prone, in general, to aggregation [8–13]. Additionally, the transition metal oxides, with charge–discharge capability based on their redox reactions, often suffer from inferior rate performance, low utilization rate and poor cycle stability even though possessing an extremely attractive theoretical capacitance value [14–17]. Among the numerous electrode materials, nickel-based ones with the advantages of natural abundance and low cost, combined with their energy storage performance in basic electrolytes and environmental compatibility, have made them one of the most promising for pseudocapacitors [18,19]. In particular, the transmission rates of ions and electrons during the charge–discharge process, which determine the specific capacitance and the rate performance of the supercapacitors, need to be mentioned. It is generally accepted that the redox reaction between the active materials and the electrolyte ions occurs only in a thin layer on the surface of the active materials [20]. The preparation of active pseudocapacitance materials with large specific surface area, porosity and good electronic conductivity is therefore highly preferred in order to enhance the performance of the supercapacitors [21,22].

In order to meet the above mentioned requirements, an effective approach may be to construct hierarchical porous structured, carbon–transition metal composites with high electrochemical performance [23]. The hierarchical porous structure generally consists of one/two dimensional nanostructures featuring a large specific surface area to provide more effective contact between the electrolyte ions and the active materials, so as to raise their utilization rate and enhance the electrochemical performance of the supercapacitors [24]. Owing to the large specific surface

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area, outstanding electronic conductivity and a two-dimensional lamellar structure [25,26], graphene sheets (GS) are usually incorporated into pseudocapacitance materials to enhance their electrochemical performance [27–30].

In this work, a series of composites based on nickel compound–graphene sheets (NiBC–GS) are prepared by flocculation of intercalated nickel dichloride–graphene oxide from a solution using hydrazine hydrate as flocculant and reductant, followed by a subsequent annealing process. The NiBC–GS designed as a loosely packed structure with GS sheets uniformly distributed in the $NiCl_2$–hydrazine complex ($Ni(N_2H_4)_xCl_2$) matrix can facilitate the efficient transport/migration of ions and are expected to possess excellent specific capacitances. More importantly, the application of the prepared $Ni(N_2H_4)_xCl_2$–GS, as an electrode composite for use in supercapacitors, is a new attempt and has not been reported by others. The texture and morphology of the obtained composites were characterized by powder X-ray diffraction (XRD), thermogravimetric analysis (TGA) and field-emission scanning electron microscopy (FESEM). In addition, the variation of specific capacitances of NiBC–GS with the annealing temperature was also studied in detail.

2. Experimental

All chemicals are analytical grade, purchased from J&K China Chemical Ltd and used as received without further purification. Graphene oxide (GO) suspension (0.1 mg mL^{-1}) was prepared by a modified Hummer's method [31,32].

Two series of samples, nickel chloride-based compounds without GS incorporation (NiBC) and with GS incorporation (NiBC–GS), were respectively prepared. In a typical procedure for preparation of NiBC–GS, 950 mg (0.004 mol) of nickel dichloride ($NiCl_2·6H_2O$) was dissolved in 150 mL of *N*,*N*-dimethylformamide (DMF) and mixed with 5.2 mL of GO (0.52 mg GO powders) suspension in DMF under stirring and ultrasonic at room temperature, followed by drop-wise addition of 2 mL of aqueous solution (80 wt%) of hydrazine hydrate ($N_2H_4·H_2O$, about 0.02 mol, making N_2H_4/Ni^{2+} at 5.0 by mole) under stirring to induce the flocculation reaction. The reaction was allowed to proceed for 30 min upon completion of the $N_2H_4·H_2O$ addition. The temperature was then increased to 80 °C and held for 30 min in order for GO in the flocculate to be reduced to GS by $N_2H_4·H_2O$. The product was rinsed twice with 100 mL of ethanol, and dried in air flow at 50 °C for 12 h to obtain NiBC–GS composite, denoted as NiBC-GS50, with the ending number indicating drying temperature. The samples denoted as NiBC-GS250 or NiBC-GS450 were obtained the same way as for NiBC-GS50, except that they were treated further after ethanol rinsing and drying at 50 °C, followed by an annealing process at 250 °C and 450 °C, respectively. This annealing was conducted by an increase in temperature at a rate of 5 °C min^{-1}, and the sample held at the target temperature for 4 h. For preparation of NiBC samples, NiBC-250 for example, the same procedure was followed without addition of GO suspension.

The structure and morphology of the composites were characterized by powder X-ray diffraction (XRD, Rigaku D/Max 2400, Cu-*Kα* radiation), thermogravimetric analysis (TGA, STA 449C, air flow) and field-emission scanning electron microscopy (FESEM, JEOL JSM-6701F). Cyclic voltammetry (CV) and galvanostatic charge/discharge experiments were carried out using a CHI 660C electrochemical workstation (Shanghai CH Instrument Company, China) in an electrolyte solution of 2.0 mol L^{-1} KOH in a three-electrode system. The working electrode was fabricated by pasting a homogeneous slurry of active material (4 mg), carbon black and poly(tetrafluoroethylene) in a mass ratio of 80:15:5 into a porous nickel foam. A platinum (Pt) sheet and an Ag/AgCl (KCl-saturated) electrode served as the counter electrode and the reference electrode, respectively. The specific capacitance was calculated according to the following equation:

$$C_m = \frac{C}{m} = \frac{I \times \Delta t}{(\Delta V \times m)} \tag{1}$$

where C_m (F g^{-1}), I (mA), Δt (s), ΔV (V) and m (mg) are the specific capacitance, charge–discharge current, discharging time, potential drop during discharge and the mass of the active material within the electrode, respectively.

3. Results and discussion

3.1. Synthesis and morphology of NiBC and NiBC–GS

A color change was observed with the addition of $N_2H_4·H_2O$ solution to the $NiCl_2$ solution in DMF for preparation of NiBC samples. This color change was dependent on the added amount of $N_2H_4·H_2O$ solution. The $NiCl_2$ solution, initially green, became purple along with an obvious generation of flocculation or precipitation when 1 mL of $N_2H_4·H_2O$ solution (80 wt%) was added to 150 mL of the $NiCl_2$ solution (containing 950 mg, *i.e.*, 0.004 mol of $NiCl_2·6H_2O$, giving N_2H_4/Ni^{2+} molar ratio of 2.5). With further addition of another 1 mL of $N_2H_4·H_2O$ solution, achieving a N_2H_4/Ni^{2+} molar ratio of 5.0, the reaction medium turned pink. Such color evolution was also previously reported for the reaction system conducted in a full aqueous medium [33,34]. The flocculate thus prepared was filtered and dried at 50 °C for 12 h to obtain a powder sample of NiBC50 with pink color. During the preparation of GS-containing samples, the same color evolution was observed, except the final flocculation composites turned black with the reduction of GO to GS by $N_2H_4·H_2O$ after raising the temperature to 80 °C and maintaining this temperature for 30 min.

Generally, different complexes can be formed by the reaction of $NiCl_2$ and $N_2H_4·H_2O$ solutions, depending on their relative amounts [34–37]. At a low N_2H_4/Ni^{2+} ratio of 2.5, $Ni(N_2H_4)_2Cl_2$ is formed with a purple color; while a pink crystal form of $Ni(N_2H_4)_3Cl_2$ can be produced at a higher N_2H_4/Ni^{2+} ratio of 5.0. It is conceivable that initially formed $Ni(N_2H_4)_2Cl_2$ may remain at the end of the reaction, although part of it is certainly transformed into the $Ni(N_2H_4)_3Cl_2$ complex. It is to point out that there is no scientific support indicating that the presence of GO or GS would interfere with the reaction between $NiCl_2$ and $N_2H_4·H_2O$; namely, the same nickel-hydrazine complexes were formed in GS incorporated NiBC. With the presence of black-colored GS, however, the color of the nickel–hydrazine complexes is masked.

To observe the morphology of the samples, NiBC50 and NiBC-GS50 were examined by FESEM (Fig. 1) and compared with pure GS (Fig. 1a), prepared by direct reduction of GO-DMF suspension using $N_2H_4·H_2O$ as the reductant at 80 °C for 30 min, followed by freezing drying. The lamellar and surface folding structures of GS are observed as expected; while only nano-sized granular particles or loosely packed aggregates are present in NiBC (Fig. 1b). With regard to the samples of NiBC-GS50 (Fig. 1c and d), the GS sheets are well dispersed in the NiBC matrix and clearly identified by the arrows. As previously reported [31], two-dimensional microstructures of GO sheets with a thickness of about 1 nm and a width of several micrometers were dispersed in DMF. In this work, uniform NiBC–GO composites should be formed by quick flocculation of $NiCl_2$–GO–DMF solution with $N_2H_4·H_2O$ addition, and uniform NiBC-GS50 composites finally obtained after *in-situ* reduction of GO and subsequent treatment.

The typical FESEM images of NiBC–GS obtained at different annealing temperatures are displayed in Fig. 2. From Fig. 2a and b, where the samples were treated by an annealing temperature at

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