Preparation of CoFe₂O₄-Graphene Composites Using Aerosol Spray Pyrolysis for Supercapacitors Application

Chongmin Lee^{1,2}, Hankwon Chang^{1,2}, Hee Dong Jang^{1,2*}

¹ Resources Utilization Research Center, Korea Institute of Geoscience and Mineral Resources, Yuseong-gu, Daejeon 34132, Korea

² Department of Nanomaterials Science and Engineering, University of Science and Technology, Yuseong-gu, Daejeon 34113, Korea

ABSTRACT

Cobalt-iron oxides have attracted much attention as electrode materials for supercapacitors. Graphene loaded with cobalt ferrite (CoFe₂O₄) nanoparticles can exhibit enhanced specific capacitance. Here, we present three-dimensional (3D) crumpled graphene (CGR) loaded with CoFe₂O₄ nanoparticles. The CoFe₂O₄-graphene composites were synthesized from a colloidal mixture of GO, FeCl₃·6H₂O, and CoCl₂·6H₂O by one step aerosol spray pyrolysis. The CoFe₂O₄-GR composites displayed a morphology resembling a crumpled paper ball, and the size of the CoFe₂O₄ and CGR in the composites was around 5 nm and 500 nm, respectively. The highest specific capacitance of the CoFe₂O₄-graphene composites was 253 F g⁻¹.

Keywords: Aerosol spray pyrolysis; CoFe₂O₄; Nanoparticles; Graphene; Supercapacitors.

INTRODUCTION

As the energy industry progresses, the development of next-generation energy storage devices is attracting attention (Zhang and Zhao, 2009). Among the energy storage devices currently under active research, supercapacitors that store energy by ion adsorption or electrochemical reaction at the interface between the electrode and the electrolyte have been of great interest because supercapacitors exhibit high power density, fast charging, and longevity (Jiang *et al.*, 2012). Their performance is mainly determined by the properties of the electrode material (Chen *et al.*, 2014). Until now, three types of electrode material have been mainly studied: carbon materials, transition metal oxides, and conductive polymers (Xia *et al.*, 2008). Among them, transition metal oxide has been widely studied as an electrode material of pseudocapacitors due to its potentially high discharge capacitance and high energy density. In

particular, cobalt oxide (Co₃O₄) has a high theoretical capacitance (1,100 F g⁻¹) and low unit cost of the electrode material for next-generation pseudocapacitors (Zhi *et al.*, 2013). However, single metal oxide-based electrode materials have drawbacks of low output and lifetime characteristics due to their low electrical conductivity (Kumbhar *et al.*, 2012). Recently, studies have been reported on the improvement of the electrical conductivity and specific capacitance of single transition metal oxides by synthesizing mixed transition metal oxides (MTMOs). Among the various MTMOs studied for use as supercapacitor electrode materials, iron-cobalt binary metal oxides are of increasing interest (Wu *et al.*, 2013). In addition, to further improve the electrochemical benefits of iron-cobalt oxides, fabrication of composite between those oxides and carbon materials is reported (Sahoo and Rout, 2016). In previous studies, He *et al.* (2013) have synthesized CoFe₂O₄-graphene (GR) composites and have introduced them as supercapacitor electrodes, showing an improvement in specific capacitance compared to GR and CoFe₂O₄. Xiao *et al.* (2014) reported a cobalt ferrite (CoFe₂O₄)-graphene nanocomposite electrode material that exhibited high Li-ion storage capacity as a cathode material in an Li-ion battery, and suggested that it can also be used as a supercapacitor electrode.

Various methods, such as the vapor phase method (Soofivand and Salavati-Niasari, 2015), hydrothermal synthesis method (Liang *et al.*, 2011), precipitation method (Li *et al.*, 2010), solid phase combustion method (Rai *et al.*, 2013), mechanochemical method (Sun and Lu, 2012),

* Corresponding author.

Tel.: +82-42-868-3612; Fax: +82-42-868-3415
E-mail address: hdjang@kigam.re.kr

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sol-gel method (Liu *et al.*, 2012), and gas condensation method (Yermakov *et al.*, 2013), have been attempted to obtain metal oxide-graphene composite powder. Among them, the liquid phase method is most widely used, and is known as a method capable of controlling the size of metal oxide nanoparticles. However, it is also known that the liquid phase method has a high manufacturing cost, and the ion diffusion behavior becomes poor due to severe aggregation of the graphene sheet, resulting in deterioration of the supercapacitor performance (Wang *et al.*, 2012). In addition, since post-heat treatment of as-synthesized particles is required, the size of the particles increases due to the agglomeration of the metal oxide nanoparticles, which has to be solved. On the other hand, aerosol spray pyrolysis (ASP), which is a vapor phase method, has merits in that the process is simple and continuous compared with the existing process. ASP also supports the coagulation degree of the produced graphene being low, and the size of the produced nanoparticles can be maintained (Wu *et al.*, 2012).

In this study, we synthesized graphene composite powders with CoFe_2O_4 oxide nanoparticles adhered to crumpled paper ball shape graphene by using ASP. The reaction temperature of ASP was chosen as a process variable for the preparation of the CoFe_2O_4 -GR composite powder. The morphology and crystal phase of CoFe_2O_4 -GR composites were observed by FE-SEM and XRD analysis according to the reaction temperature. The electrochemical performances of the CoFe_2O_4 -GR composites were investigated by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS).

METHODS

Fabrication of CoFe_2O_4 -Graphene Composite

Graphene oxide (GO) was prepared by a modified Hummers' method and then dispersed in distilled water (Hummers and Offeman, 1958). The GO colloid solution and the metal precursor ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) were mixed while the GO concentration was 0.5 wt%, and the weight ratio of the metal precursor/GO was 0.3. The colloidal mixture was then sprayed and introduced into the tube furnace under conditions of a reactor temperature of 400°C and a flow rate of 10 L min^{-1} of the carrier gas to prepare a CoFe_2O_4 -GR composite. A schematic diagram of the ASP process for preparing the CoFe_2O_4 -GR composite is shown in Fig. 1. The apparatus for fabricating the

composite consisted of an ultrasonic atomizer for spraying the precursor, a tube furnace for synthesis of the composite, and a filter to collect products. An industrial ultrasonic atomizer contained six 1.7 MHz vibrators. In order to prevent the heat generated by the vibrator during the droplet spraying, cooling water was introduced at a constant flow rate (20 mL min^{-1}), and the temperature was kept below 20°C . The tube furnace employed a cylindrical quartz tube with a diameter and length of 70 mm and 1400 mm, respectively. The GO and the metal precursor coexist in the micron-sized sprayed droplets generated from the colloid mixture of GO and metal precursor ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$). As these droplets pass through the tube furnace, water as a solvent inside the droplet evaporates, and self-assembly of the metal precursor and crumpling of the GO sheet occur. The ASP process can be mass-produced easily and quickly in a single continuous process at the time of producing the composite, and it has the advantage that a reducing agent is not needed because the GO can be reduced into GR by the heat applied when the CoFe_2O_4 -graphene composites are fabricated. Therefore, GO and metal precursors ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) are simultaneously reduced and oxidized at predetermined temperatures, resulting in the formation of CoFe_2O_4 nanoparticles loaded with crumpled GR composites.

Supercapacitor Electrode Fabrication

In order to evaluate the electrochemical performance of supercapacitors, the synthesized CoFe_2O_4 -graphene composite powder was employed as an electrode active material, and polyvinylidene difluoride (PVDF) was used as a binder. The composite and PVDF powders were mixed in a weight ratio of 9:1 with *N*-methyl-2-pyrrolidone (NMP) solvent, followed by stirring for 20 minutes to prepare a slurry. The prepared slurry was coated on carbon paper by the Doctor Blade method, dried in an 80°C vacuum oven for 2 hours, and then the paper was cut with a diameter of 14 mm for each electrode. The supercapacitor cell was assembled using a two-electrode HS Flat Cell (Hohsen Corp., Japan) with a separator (GF/C, Whatman).

Analysis

In order to observe the morphology of the CoFe_2O_4 -GR composites prepared in this study, field-emission scanning electron microscopy (FE-SEM; Sirion, FEI) and X-ray diffraction (XRD; RTP 300RC, Rigaku) were used to

Fig. 1. Schematic illustration of the formation of CoFe_2O_4 -graphene composites from colloidal mixture of metal precursor and graphene oxide via aerosol spray pyrolysis.

measure the morphology and the crystal phase of the composite, respectively. Cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) were measured using a potentiostat (VSP, Bio-logics) to evaluate the electrochemical properties of the supercapacitor electrode composed of CoFe₂O₄-GR composite. The electrochemical characteristics were measured by scanning a potential range of −0.2 to 0.8 V using a two-electrode system under a 5 M KOH electrolyte. From the charge/discharge behavior measurement, the specific capacitance (C) was calculated based on the discharge process of the electrode.

Eq. (1) for the calculation of the non-volatile capacity is as follows:

$$C = \frac{2 \times I \times \Delta t}{m \times \Delta V} \quad (1)$$

where I is the current (A), m is the weight (g) of the CoFe₂O₄-graphene composite powder, ΔV is the potential range (V) during the discharge process, and Δt is the discharge time (s) (Mastragostino *et al.*, 2002).

RESULTS AND DISCUSSION

Characterization of CoFe₂O₄-Graphene Composites

Fig. 2 shows the SEM images of the CoFe₂O₄-GR composite powders prepared by ASP. SEM images showed that the CoFe₂O₄-graphene composite prepared in Ar atmosphere appeared as three-dimensional crumpled morphology, and the average particle size was about 600 nm. It was also confirmed that CoFe₂O₄ nanoparticles having a size of about 5 to 10 nm adhered to the surface of the crumpled paper-like graphene. As the reaction temperature increased, the size of the CoFe₂O₄ nanoparticles deposited on the graphene surface increased. The size distribution of

CoFe₂O₄-graphene composites calculated from the SEM images is shown in Fig. 3. The average particle size of CoFe₂O₄-graphene composite decreased from 760 nm to 540 nm as the reaction temperature increased from 300°C to 500°C. The size of the composites can be tuned by capillary force applied to GR in the sprayed droplets while solvent evaporated. Then, high capillary force originating from the high temperature could form crumpled morphology of composites with smaller size. Fig. 4 shows the results of XRD analysis of the CoFe₂O₄-graphene composite prepared by the ASP process. The peak intensity corresponding to the cobalt ferrite crystal phase increased with the increase of the reaction temperature. The broad peaks near 23.5° and 42.9° are considered to be peaks corresponding to the typical graphene crystal type with the graphite peak shifted to the left. As the reaction temperature increased, the XRD peak corresponding to graphene showed a shift to the left of the graphite peak. This is because the cobalt ferrite nanoparticles introduced into the graphene surface increased the interlayer spacing as well.

Electrochemical Properties of CoFe₂O₄-GR Electrodes

In order to investigate electrochemical properties at the interface between the electrolyte and the CoFe₂O₄-graphene composite, electrodes were fabricated using CoFe₂O₄-GR composite powders prepared at reaction temperatures of 300°C. The results of cyclic voltammogram (CV) measurement using two electrodes after impregnation with KOH electrolyte are shown in Fig. 5. The scan rate was 10 mV s^{−1}, and the voltage range was 0–1 V. The electrode fabricated with the CoFe₂O₄-GR composite showed a weak, broad peak at around 0.4 V due to the oxidation-reduction reaction of the CoFe₂O₄ nanoparticles attached to the graphene surface. From the CV results, it is noted that the CoFe₂O₄-GR composite electrode showed the electrochemical behavior of the pseudocapacitor. Fig. 6(a)

Fig. 2. SEM images of the CoFe₂O₄-graphene composites prepared at different reaction temperatures of (a, d) 300°C, (b, e) 400°C, and (c, f) 500°C.

Fig. 3. Size distributions of CoFe₂O₄-graphene composites at different reaction temperatures of 300°C (a, d), 400°C (b, e), and 500°C (c, f).

Fig. 4. X-ray diffraction patterns of the CoFe₂O₄-graphene composites prepared at different reaction temperatures.

Fig. 5. Cyclic voltammetry curves of the CoFe₂O₄-graphene composites prepared at different reaction temperatures.

shows a galvanostatic charge/discharge (GCD) graph of the CoFe₂O₄-GR composite electrode measured at 5 M KOH electrolyte at a potential range of -0.2 to 0.8 V. Comparing the GCD of the CoFe₂O₄-graphene composite electrode measured by increasing the current density, the composite electrode fabricated at each reaction temperature

showed a symmetrical triangular shape. The specific capacitance of the CoFe₂O₄-graphene composite electrode prepared at GCD at 300, 400, and 500°C was calculated using Eq. (1), and is shown in Fig. 6(b), respectively. At the current density of 0.1 A g^{-1} , the specific capacitance of CoFe₂O₄-GR composites showed the highest specific capacitance at 253 F g^{-1} at reaction temperature of 400°C. At 500°C, the lowest specific capacitance is observed at F g^{-1} . As the reaction temperature increased, the specific surface area and electrical conductivity of the CoFe₂O₄-GR composite decreased as the size of the CoFe₂O₄ nanoparticles grown on the graphene surface increased. It was found that CoFe₂O₄-GR composites prepared at the reaction temperature of 300°C showed the lowest specific capacitance at 400°C even though the size of the CoFe₂O₄ nanoparticles was smaller than other samples. This is because 300°C is insufficient to reduce the graphene oxide, which reduces the electrical conductivity of the CoFe₂O₄-GR composite due to hydroxyl groups remaining on the graphene surface. Fig. 7 shows the Nyquist plot measured by electrochemical impedance spectroscopy (EIS). The enlarged graph of Fig. 7 depicts the high-frequency part of the semicircle. The part where the semicircle and the real axis intersect is related to the electrical conductivity of the electrode by series resistance. The diameter of the semicircle represents

Fig. 6. Galvanostatic charge/discharge curves of the CoFe_2O_4 -graphene composites prepared at different reaction temperatures.

Fig. 7. Nyquist plot of the CoFe_2O_4 -graphene composites prepared at different reaction temperatures.

the area of the reaction site by charge transfer resistance. As the reaction temperature increased, the series resistance increased. In other words, the electric conductivity decreased. It was found that the reaction temperature of 400 °C showed the smallest diameter of semicircle. Following that, the higher electrical conductivity of the composite fabricated at 400 °C can be obtained (Xu *et al.*, 2010).

CONCLUSIONS

We successfully synthesized a CoFe_2O_4 -graphene composite powder using the ASP process. FE-SEM analysis revealed that the composites were shaped like three-dimensional crumpled particles, and the degree of wrinkling increased with the reaction temperature. The crystal phase of the metal oxide nanoparticles adhered to the graphene surface was identified as cobalt ferrite (CoFe_2O_4), and the crystal size increased as the reaction temperature increased. As a result, the electrode fabricated with CoFe_2O_4 -graphene composites at 400 °C was found to have the highest specific capacitance, 253 F g^{-1} , and a rate capability of 80.5% at a

current density of 4 A g^{-1} . Overall, a nanocomposite electrode of CoFe_2O_4 nanoparticles and graphene improves the electrochemical characteristics of electrostatic capacity and charge/discharge efficiency in a supercapacitor by increasing the ion and electric conductivity. Based on these results, CoFe_2O_4 -GR composite powder is a promising new supercapacitor electrode material.

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DISCLAIMER

The authors declare no conflicts of interest.

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