



Graphene and maghemite composites based supercapacitors delivering high volumetric capacitance and extraordinary cycling stability



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ABSTRACT

Metal oxides (like MnO_2 , Fe_2O_3 , and Co_3O_4 , etc) based supercapacitors have disadvantages, such as low volumetric capacitance for thick-film electrodes, or short cycling life because a Faradaic process involves chemical changes of state of the reactant species. In the present work, we report that supercapacitors based on reduced graphene oxide and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) composites (G γ M) exhibit superior performance. G γ M electrodes with average electrode thickness up to $\sim 60\ \mu\text{m}$ have a high volumetric capacitance of $230\ \text{F cm}^{-3}$, together with an outstanding electrode package density of $1.44\ \text{g cm}^{-3}$. Particularly, the G γ M electrodes have excellent cycling performance of $\sim 90\%$ capacitance retention over 100,000 galvanostatic charge–discharge cycles or voltage floating at 0.9 V for 300 h. No detectable change in phase and an effective inhibition of $\gamma\text{-Fe}_2\text{O}_3$ refinement after cycle-life test are confirmed by X-ray diffraction and transmission electron microscopy.

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1. Introduction

Metal oxides have great potential application in supercapacitor due to their high theoretical capacitance which is established on the basis of Faraday Effect [1,2]. In general, the supercapacitor consists of two categories determined by different storage principles. One is the electrical double layer capacitors (EDLCs) represented by Helmholtz interface capacitor; the other is pseudocapacitors based on Faradaic reaction, which occurs at or near the surface of electrode materials through electrochemical adsorption/desorption or redox reaction [3]. RuO_2 is an ideal candidate for supercapacitor application but is prohibited by high cost. Some transition metal oxides like MnO_2 , Fe_2O_3 , and Co_3O_4 , etc are now quite active due to their low cost, high theoretical capacitance and environmental friendliness [4–6]. However, these metal oxides still present some major drawbacks (e.g. low electrical conductivity, poor stability, and high self-discharge) which preclude an industrial utilization.

EDLCs have lifetimes of 10 or more years or cycle life of more than 500,000 cycles, which compensates for its relatively low energy density [7]. Although pseudocapacitance can reach 10–

100 times higher than that of EDLCs [8], it usually suffers from low stability. One of the main reasons is that the storage charge mechanism of EDLCs and pseudocapacitors is different. The former arises from the potential-dependence of the surface density of charges stored electrostatically at the interface of the electrodes; the latter is Faradaic in origin, involving the passage of charge across the double layer. Another possible reason for poor cycling stability is volume expansion. One to two electrons transfer per atom happens during Faradaic reaction, while only ~ 0.18 electron per atom is stored in the double-layer; therefore, the volume effect is larger for pseudocapacitance [9]. This effect refines the grains, degrades electrode materials, and induces the stress or crack, which are harmful to the cycling stability.

Besides the cycling life, the package density of the electrode is also a key parameter in order to get a compact electrode. Activated carbon electrode usually has a package density of $0.5\text{--}0.7\ \text{g cm}^{-3}$, and the value further decreases to $0.1\text{--}0.5\ \text{g cm}^{-3}$ for carbon nanotube and graphene [10–12]. Low density, porous structure, and presence of defects cause low gravity package density of nanocarbon electrodes. At a high pressure of even 25 t applied to compact graphene electrode, a moderate value of $0.75\ \text{g cm}^{-3}$ was obtained [13]. Recently, the package density of $>1.0\ \text{g cm}^{-3}$ was reported for graphene electrodes [14–16]. However, these work used complicated technology process that resulted in high-cost and were difficult to scale-up. In comparison with carbon

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materials, metal oxides are superior in package density because of their high density. Unfortunately, this advantage is restricted by their low electrical conductivity and surface redox in nature, which causes that thick metal oxide electrodes have low volumetric capacitance [17,18]. For alleviating these problems, coated a thin carbon film out of metal oxide particles or composited with carbon materials were introduced [19–22]. However, there are rare reports in the literature of volumetric capacitance for thick pseudocapacitor electrodes whose cycling stability is also inferior to than that of EDLCs.

In the present work, we reported that reduced graphene oxide (RGO) supported maghemite (γ -Fe₂O₃) composite (G γ M) electrodes with the loading mass comparable to practical application show high volumetric capacitance of $\sim 230 \text{ F cm}^{-3}$, high package density of $1.44 \pm 0.01 \text{ g cm}^{-3}$, and excellent cycling stability. The γ -Fe₂O₃ nanoparticles are incorporated into graphene nanosheets by chemical decoration of graphene and thermal treatment. It is interesting that single phase of γ -Fe₂O₃ magnetic nanoparticles is prepared by this simple method without using some special conditions like dramatic heat treatments, strong magnetic field treatment, or organic molecules protection.

2. Experimental Section

2.1. Sample preparation

Graphite oxide (GO) was prepared using modified Hummer's method and have been reported elsewhere [23]. GO (2 g L^{-1})/FeCl₃·6H₂O (64 g L^{-1}) = 4:1 (volume ratio) were dispersed by ultrasonication prior to Fe³⁺ ions decorated GO was obtained through magnetic stirring for several hours. Then the water and surplus Fe³⁺ ions were removed through vacuum filtration. The obtained samples were put into high-purity Al₂O₃ crucible and heat-treated at 350 °C for 2 h in argon atmosphere with a gas flow of 160 sccm. The resulted powder was washed for several times by deionized water and alcohol. And then the powder was dried at 60 °C for 48 h. Finally, G γ M were synthesized and used for characterizations and electrochemical measurements.

2.2. Characterization

SEM images and EDX detection were obtained by a Hitachi S-4300 scanning electron microscope. TEM and selected area electron diffraction (SAED) characterizations were performed with a JEOL JSM-2010. XRD data of composites was collected with a Rigaku Dmax 2500 diffractometer with Cu radiation between 5 and 70° at a scan rate of 8°/min. XPS analysis was measured with a PHI Quantar SXM (ULVAC-PHINC). BET surface area and Barrett-Joyner-Halenda pore size distribution measurements of G γ M samples were carried out with Micromeritics ASAP 2020 surface area analyzer using N₂ gas adsorption-desorption isotherm at -196 °C. Magnetic properties were detected on Quantum Design PPMS (PPMS-9).

2.3. Supercapacitor electrodes preparation and measurements

For symmetric supercapacitors, 2032 type coin cells were used. 85 wt% of the G γ M, 7 wt% PTFE (60 wt% dispersed in water), and 8 wt% super C45 were firstly dispersed in isopropanol by supersonic dispersion. The obtained slurry was heated at 80 °C to remove excess isopropanol and then kneaded thoroughly and rolled down to 90–100 μm thick films. After drying for 24 h at 120 °C, the films were pressed onto 60 μm -thickness stainless steel mesh or 30 μm -thickness titanium foils and then punched into 1.3 cm diameter electrodes. Then the electrode plates were mechanically compacted. The thickness of electrode with titanium

foil as the current collector is 55–65 μm . The areal loading mass of a single electrode is $10.5 \pm 1.0 \text{ mg}$.

Cyclic voltammetry (CV) curves and electrochemical impedance spectroscopy (EIS) plots were measured using AutoLab PGSTAT302 N equipment. EIS was obtained at the frequency range from 100,000 to 0.01 Hz with a 10-mV voltage amplitude at open circuit voltage. Galvanostatic charge-discharge (GCD) process and cycle-life test was measured on an Arbin MSTAT4 multi-channel galvanostat/potentiostat instrument.

3. Results and Discussion

3.1. Morphologies and compositions of G γ M samples

GO is a layered stack of puckered sheets and contains many oxygen functionalized groups like hydroxyl, epoxy, and carboxyl [24]. These functionalized groups severely degrade the electrical performances like electrical conductivity but make GO a good candidate for the synthesis of composite materials. The platelet morphology is maintained as shown in Fig. 1(a) when oxygen functionalized groups have been removed and γ -Fe₂O₃ nanoparticles are incorporated. SEM images indicate that G γ M has a uniform morphology that is plate-like particles. The average weight ratio of γ -Fe₂O₃ nanoparticles in G γ M sample is about 32 wt% by EDX detection (Supplementary Fig. S1). TEM characterization further shows that γ -Fe₂O₃ nanoparticles are well dispersed on the surface of RGO (see Fig. 1(b)). The average particle size of γ -Fe₂O₃ is $\sim 20 \text{ nm}$. On the basis of calibrating by Au standard diffraction data using external standard method, we confirmed that five diffraction rings corresponded to interplanar spacing of 2.98, 2.51, 2.09, 1.63, and 1.48 Å, respectively, which were consistent with the Miller indices (2 2 0), (3 1 1), (4 0 0), (5 1 1), and (4 4 0) of γ -Fe₂O₃ (JCPDS No: 39-1346), (see Fig. 1(c)). After thermal reduction, the resulted graphene is aggregated to some extent and G γ M has a BET surface area of $\sim 40 \text{ m}^2 \text{ g}^{-1}$ (Supplementary Fig. S2). Some γ -Fe₂O₃ nanoparticles are pinned into the lattice of graphene as shown by high-resolution TEM of Fig. 1(d). Fig. 1(e) displays (2 2 0) plane with a interplanar spacing of 2.98 Å using line interception method of Fig. 1(d) marked by white arrows.

In order to further clarify the structure of G γ M, we carried out more characterizations. After thermal treatment, the GO was reduced and Fe³⁺ ions transformed into γ -Fe₂O₃ as indicated by XRD pattern (Fig. 2(a)). A strong but broad diffraction peak locating at $2\theta = 25.03^\circ$ is corresponding to the (2 0 0) plane of graphite. All the other diffraction peaks with 2θ degree at 30.211, 35.603, 43.191, 53.675, 57.220, and 62.761° can be indexed to (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), (4 4 0) surfaces, which belong to γ -Fe₂O₃ phase. These diffraction peaks are in line with the standard data of γ -Fe₂O₃ phase (JCPDS No: 39-1346), which is marked by the red line in Fig. 2(a). In contrast, GO and Fe³⁺ ion decorated GO without heat-treatment only display one diffraction peak at $2\theta \approx 11.63^\circ$ (Supplementary Fig. S3).

Most of the oxygen content bonded with carbon atom is reduced as shown in Fig. 2(a). Since γ -Fe₂O₃ contains oxygen element, the strict ratio of C/O in RGO is hard to determine. The C1s spectrum shows a sharp peak at 284.8 eV accompanied by some small peaks of oxygen functionalized groups, similar to other graphene material like chemically reduced graphene and bottom-up method yielded graphene [25–27]. The Fe 2p_{1/2} and 2p_{3/2} peaks locate at 711.4 and 724.9 eV (see Fig. 2(b)), which are consistent with Fe₂O₃ phase. Furthermore, a satellite peak at 718.1 eV is a characteristic of Fe³⁺ ions in γ -Fe₂O₃ [28]. Besides, O1s spectrum also splits into two peaks using Lorentzian–Gaussian (80%:20%) to fit the measured data, which is coincide with different chemical bonding states of oxygen element in RGO and γ -Fe₂O₃

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