Electrochemically reduced graphene oxides/nanostructured iron oxides as binder-free electrodes for supercapacitors

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In this work, a facile approach was applied to prepare composites of electrochemically reduced graphene (ecrGO) oxides and iron oxides (FeOx) as binder-free electrodes for enhancing the electrochemical performance of supercapacitors. The iron oxides were intercalated between the graphene oxides sheets to form sandwich-like composites, such composites were electrochemically reduced in an alkaline solution and directly used as electrodes without any binders. The as-obtained composite (ecrGO/FeOx) shows a good mechanical strength according to the SEM and Raman results, also exhibits high specific capacitance (Csp) of ~235 F g⁻¹ at a scan rate of 10 mV s⁻¹ and good cycling stability of 92% retention after 2000 cycles in 1 M NaOH. Although there is a decline of Csp for the ecrGO/FeOx composite because of the high charge transfer resistance and poor conductivity of the iron oxides, it still possesses a higher Csp than ecrGO when the scan rate increases to 400 mV s⁻¹. The relative high Csp and good stability of ecrGO/iron oxides composites due to the synergistic effect between ecrGO and iron oxides during the electrochemical processes, indicates it can be a promising candidate for supercapacitors.

1. Introduction

The supercapacitor, also called the electrochemical capacitor, is considered to be a promising energy storage device due to its high power density, and fast charging and discharging. The mechanism of a supercapacitor involves a double layer capacitor with physical adsorption-de-adsorption and a pseudocapacitor with fast reversible redox reactions [1]. Carbonaceous materials, such as activated carbon, carbon nanotubes, carbon fibers and graphene, have been widely investigated for supercapacitors because of their good chemical stability, mechanical strength and conductivity [2-4]. The pseudocapacitors originate from faradic redox reactions of electrode materials like conducting polymers [5,6] or transition metal oxides [7,8].

Graphene has been widely applied in supercapacitors due to the large surface area and high conductivity [9]. However, the experimental measured capacity of graphene is much lower than theoretical value, this is because graphene sheets obtained from the reduction of graphene oxides (GO) easily stack together, resulting in the decrease of surface area and the difficulty for the ions permeating to the surface of graphene [10]. Therefore, graphene-based composites have been developed to facilitate the ion permeability to electrode surface by modifying graphene sheets with carbon materials or metal oxides [11-14].

In terms of metal oxides, iron oxides have been received considerable attention for use in supercapacitors, due to their low toxicity, natural abundance, environmental friendliness, and chemical and thermodynamical stability [1]. In addition, iron oxides have higher potential for hydrogen evolution in aqueous solutions in contrast with other metal oxides (e.g. nickel oxides or manganese oxides) [15,16]. Also, the pseudocapacitance of the iron oxides can be generated during processes of charge and discharge. These make iron oxide a promising alternative material as an electrode in an aqueous solution for supercapacitors.

In this study, graphene oxide (GO) as graphene precursor and iron oxides as “spacers” were used to obtain the binder-free electrode for supercapacitors, wherein iron oxides can avoid the graphene sheets stacking after being reduced from GO, and also can introduce pseudocapacitance to overall capacitance of graphene based composites. GO can homogenously disperse in water due to the hydrophilicity of the polar functional groups [17], and these functional groups (such as —COOH and —OH) can make the

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positively charged iron oxides dispersion uniformly adhere to GO sheets. Also the GO can form membrane after drying, so it can serve like a binder to the composites without adding other binders (such as PTFE, PVDF, carbon black). These are the reasons for using GO as graphene precursors.

To achieve better conductivity, GO with poor conductivity [18] are usually reduced to graphene for supercapacitors. Chemical reduction [19], hydrothermal [15,20] or anaerobic thermal [21] reduction are widespread approaches for reducing GO. However, these methods are complicated, also special facilities are required. The electrochemical reduction applied in this study is more facile, low-cost and environmentally friendly without the reduction agents, high temperature or vacuum treatment. In addition, the electrochemically reduced GO (ecrGO) can also be directly used as electrodes, dispensing with washing or drying after the reduction process.

In this work, a facile strategy to fabricate a sandwich-like composite of ecrGO/FeOx as a binder-free electrode for supercapacitors was reported, and the schematic illustration for fabricating electrodes is shown in Fig. 1. The morphology and chemical structure of ecrGO/nanostructured iron oxides composites were investigated using field-emission scanning electronic microscopy (SEM), X-ray diffraction (XRD), Raman, and X-ray Photoelectron spectroscopy (XPS). Also the electrochemical performance of ecrGO/FeOx composites after electrochemical reduction was measured in alkaline solutions.

2. Experimental

2.1. Synthesis of Fe2O3 nanoparticles

1.35 g of FeCl3·6H2O was dissolved in 60 mL of DI water to obtain a yellow solution. The 5 mL of NH4·H2O was slowly added to the FeCl3 solution, continuously stirring for 20 min, after which a brown precipitates Fe(OH)3 was generated. This brown precipitate was transferred into a 100 mL Teflon-lined stainless steel autoclave, and was subjected to thermal dehydration at 180 °C for 12 h. After cooling to room temperature, the resulting reddish brown paste were washed with distilled water and ethanol for several times, and dried in a vacuum oven at 60 °C. Finally, Fe2O3 powder was obtained.

2.2. Preparation of ecrGO/FeOx electrode

Graphene oxide (5 g L−1, 79% carbon and 20% oxygen) was received from the Graphene-supermarket Inc., USA. 5 g L−1 of GO was diluted to 1 g L−1 with DI water in a 5-min ultrasonic process. 1 g L−1 of Fe2O3 suspension was added into the 1 g L−1 GO solution with a mass ratio of 1:1, and the mixture was subjected to ultrasonic processing for 30 min, so the Fe2O3 was uniformly distributed on the GO sheets. A platinum plate, as a current collector, was covered by the suspension of GO and Fe2O3, and dried at 150 °C for 8 min to form the binder-free GO/Fe2O3 electrode. The mass loading of the GO/Fe2O3 composites on the working electrode was around 3.8 mg cm−2.

Electrochemical reduction of GO/Fe2O3 composites with cyclic voltammetry (−1.2 V~0 V) at a scan rate of 50 mV s−1 in 1 M NaOH was carried out using a VersaSTAT potentiostat/galvanostat (Princeton Applied Research, USA) to obtain the composites of electrochemically reduced GO/FeOx. A three-electrode system with platinum wire as the counter electrode and Ag/AgCl as the reference electrode was applied.

2.3. Materials characterization

The morphology of the iron oxide nanoparticles and GO/Fe2O3 composites before and after reduction was characterized by field-emission scanning electronic microscopy (FE-SEM, JEOL JSM-6335F). The phase structure of the iron oxides was detected by an X-ray diffraction (XRD) system (PAN-alytical), ranging from 20° to 70° at a scan rate of 5° min−1. Raman scattering spectra were obtained on a MicroRaman/Phololuminescence spectrometer (Renishaw InVia) with a 633 nm Ar ion laser. X-ray Photoelectron spectroscopy (XPS) on GO/Fe2O3 composites before and after electrochemical reduction was conducted using an Axis Ultra DLD X-ray photoelectron spectrometer (Kratos) with an Al K X-ray source. The binding energy was calibrated using C 1s peak at 284.5 eV.

![Fig. 1. Schematic illustration for fabricating ecrGO/Fe2O3 electrodes.](image-url)
2.4. Electrochemical measurements

The electrochemical performance of the composites was measured in 1 M NaOH using a VersaSTAT potentiostat/galvanostat (Princeton Applied Research, USA), with platinum wire as the counter electrode and Ag/AgCl as the reference electrode. Cyclic voltammetry (CV), galvanostatic charge-discharge at various current densities and electrochemical impedance spectroscopy (EIS) of the composites were carried out. EIS was applied in a frequency range from 100 kHz to 0.1 Hz with AC amplitude of 5 mV at open-circuit potential.

3. Results and discussion

3.1. Formation of ecrGO/FeOₓ electrode by electrochemical reduction

A schematic illustration for fabricating sandwich-like ecrGO/Fe₂O₃ electrodes is shown in Fig. 1. After ultrasonic processing, a uniform suspension of as-received GO sheets and as-synthesized Fe₂O₃ particles was obtained. Here, the GO sheets serve as “scaffolds” for anchoring the Fe₂O₃ particles, and the Fe₂O₃ nanoparticles intercalating between GO sheets can in turn prevent stacking of the graphene sheets when GO is reduced.

Fig. 2. (a) CV curves of GO and GO/Fe₂O₃ composites in 1 M NaOH from −1.2 V to 0 V (vs.Ag/AgCl) at a scan rate of 50 mV s⁻¹; (b) the specific capacitance of GO and GO/Fe₂O₃ composites in 1 M NaOH as a function of the number of reduction cycles; (c) images of GO/Fe₂O₃ composites before and after electrochemical reduction.
After being coated on the platinum plate, the GO/Fe₂O₃ composites are electrochemically reduced into ecrGO/FeOₓ composites and then directly used as electrodes, without any binders.

The electrochemical reduction of GO/Fe₂O₃ composites was carried out using the cyclic voltammetry with a potential range from −1.2 V to 0 V and a scan rate of 50 mV s⁻¹. Fig. 2a shows the CV performance of the GO, Fe₂O₃ and GO/Fe₂O₃ composites during electrochemical reduction in 1 M NaOH at a scan rate of 50 mV s⁻¹. The current densities of GO (the red line in Fig. 2a) and GO/Fe₂O₃ composites (black line in Fig. 2a) increase, along with the number of reduction cycles. As reported in our previous study [22], some functional groups containing oxygen (like C——O——C, —COOH and C—OH) can be reduced by electrochemical reduction, π bonds form. Electrons can transfer via these π bonds of carbon materials, so the GO current increases with increasing numbers of reduction cycles. For the GO/Fe₂O₃ composites, in addition to the increasing current density resulting from the ecrGO formation, a pair of redox peaks appears along with the number of reduction cycles. During negative scanning, reduction peaks appear at −1.15 V due to the electrochemical reduction from Fe³⁺ to Fe²⁺. During positive scanning, oxidation peaks arise at −0.7 V because of the oxidation from Fe²⁺ to Fe³⁺ [23,24]. The pair of redox peaks become nearly stable after 150 cycles, and is attributed to the redox equilibrium between Fe²⁺ and Fe³⁺. While the current density of Fe₂O₃ has little increase as shown in the insert of Fig. 2a, when compared with GO and GO/Fe₂O₃. This is because iron oxides are almost non-conductive (the large resistance of Fe₂O₃ is provided from EIS spectra in Fig. S1), it is hard for Fe₂O₃ to capture electrons to be reduced. As a result, a better capacitive performance of the GO/Fe₂O₃ composites than the constituents (GO or Fe₂O₃) may be due to the synergistic effect between GO and Fe₂O₃ during the electrochemical reduction. On one hand, GO sheets scattered with Fe₂O₃ particles facilitates electrons or ions transferring to Fe₂O₃, so that redox reaction of Fe₂O₃ can occur more easily. On the other, intercalation of Fe₂O₃ between GO sheets can avoid stack of GO during electrochemical reduction, more charges can be adsorbed on the surface of the composite.

The specific capacitance can be calculated based on the CV curve, using the following equation [25],

$$C_{sp} = \frac{1}{m(V_f - V_i)} \int_{V_i}^{V_f} I(V) dV$$

where $C_{sp}$ is the specific capacitance (F g⁻¹), $m$ is the mass loading of material on the current collector, $V$ is the potential scan rate (V s⁻¹), $(V_f - V_i)$ is the sweep potential range (V), and $I(V)$ denote the response current (A). Fig. 2b shows the specific capacitance ($C_{sp}$) of GO and GO/Fe₂O₃ composites in 1 M NaOH with the number of reduction cycles. The $C_{sp}$ of GO increases from the initial $C_{sp}$ of 5 F g⁻¹ to 89 F g⁻¹, and becomes stable after 100 reduction cycles. This capacity improvement of GO is mainly from the conductive ecrGO. The specific capacitance of the ecrGO/FeOₓ composite becomes stable at 140 F g⁻¹, after undergoing 120 reduction cycles, and the pseudo-capacitance generated from the reversible redox reaction between Fe²⁺ and Fe³⁺ makes a large contribution to the overall capacity of the ecrGO/Fe₂O₃ composite. Fig. 2c shows images of GO/Fe₂O₃ composites before (left) and after (right) electrochemical reduction. The color of the GO/Fe₂O₃ composites turns from dark brown before electrochemical reduction to grey luster after electrochemical reduction, and the surface of the electrodes remains flat after the electrochemical reduction. It demonstrates that the ecrGO/Fe₂O₃ composites can be used as binder-free electrodes. Herein, in order to achieve better capacitive performance during electrochemical measurements, the GO/Fe₂O₃ composites applied as binder-free electrodes in this study were subjected to 120 cycles of electrochemical reduction to obtain the ecrGO/FeOₓ composites.

Fig. 3. SEM images of (a) iron oxides with its XRD pattern (inset); (b) cross profile of GO/Fe₂O₃ composites with sandwich-like structure; GO/Fe₂O₃ composites (c) before and (d) after electrochemical reduction.
3.2. Structural characterization of Fe$_2$O$_3$, GO/Fe$_2$O$_3$ and ecrGO/FeO$_x$ composites

Fig. 3a–c shows the SEM images of the Fe$_2$O$_3$ (Fig. 3a), GO/Fe$_2$O$_3$ composites (Fig. 3b) and ecrGO/FeO$_x$ composites before and after electrochemical reduction (Fig. 3c and d respectively). The synthesized iron oxides are spherical particles with uniform size around ~70 nm, as shown in Fig. 3a. Their crystal phase should be Fe$_2$O$_3$, demonstrated by the XRD results with reflections of (012), (104), (110), (112), (024), (116), (122), (214) and (300) (Fig. 2a, inset) [1,26]. Fig. 3b shows the cross sectional profile of the GO/Fe$_2$O$_3$ composites, with Fe$_2$O$_3$ nano-particles (indicated by black arrow) inserted between the GO sheets to form sandwich-like structure. Fig. 3c and d show the surface morphology of the GO/Fe$_2$O$_3$ composites before and after electrochemical reduction respectively. It can be clearly seen in Fig. 3c that the GO sheets are uniformly dark films with some wrinkles, and Fe$_2$O$_3$ particles are isolated on GO sheets. After electrochemical reduction, the iron oxide particles are still uniformly anchored on the ecrGO sheets, as shown in Fig. 3d, it demonstrates that the ecrGO/FeO$_x$ composites exhibit the good mechanical stability.

Fig. 4 shows the Raman spectra of the GO, GO/Fe$_2$O$_3$ composites before and after electrochemical reduction. It reveals the characteristic peaks of the D band at ~1340 cm$^{-1}$ corresponding to the vibration of sp3 carbon atoms of the structural defects (such as vacancies, grain boundaries) and disorder, and the G band at ~1580 cm$^{-1}$ indicating in-plane vibration of the sp$^2$ carbon atoms [11,22,27,28]. The ratio of I$_D$: I$_G$ for GO is 1.08, and this ratio increases to 1.47 for the GO/Fe$_2$O$_3$ composite, meaning a higher disorder degree of the GO/Fe$_2$O$_3$ composite than for GO. After being electrochemically reduced, the ratio of I$_D$: I$_C$ for the ecrGO/FeO$_x$ composite further increases to 1.73. Usually, after reduction of GO, the intensity ratio of I$_D$:I$_C$ was found to be higher than that of GO without reduction in many reported works [29–31]. The higher I$_D$: I$_C$ ratio of ecrGO than GO may be related to the higher disorder degree [32,33], defects [34] and smaller average size of sp$^2$ domain [34–36]. During the electrochemical reduction of GO, the vacant lattice sites are produced due to the removal of oxygenated functional groups in GO. So the defects in reduced GO may not decrease, when compared with GO without reduction [32]. Also, the increased I$_D$:I$_C$ ratio of reduced GO may be resulted from the decrease in the average size of sp$^2$ domain [36,37]. Researchers ascribed this observation to the formation of a new graphitic domain with smaller size but greater in numbers [37–40]. These may be the reasons to result in the increased intensity ratio of I$_D$:I$_C$ for reduced GO. The characteristic peaks at 217 cm$^{-1}$, 282 cm$^{-1}$, 405 cm$^{-1}$, 499 cm$^{-1}$, and 615 cm$^{-1}$ of both the GO/Fe$_2$O$_3$ composites and ecrGO/FeO$_x$ composites can be observed in Fig. 4, corresponding to the A$_{1g}(1)$, E$_{2g}$ + E$_{3g}$, A$_{1g}(2)$ and E$_{5g}$ modes of Fe$_2$O$_3$ [41]. It illustrates that iron oxide particles are successfully anchored on the GO sheets, and this Raman spectrum is consistent with the XRD result (insert of Fig. 3a). Also, the Raman patterns of the Fe$_2$O$_3$ in the composites before and after electrochemical reduction are almost the same, as black arrows in Fig. 4, indicating the good mechanical stability of the Fe$_2$O$_3$ particles before and after electrochemical reduction.

X-ray photoelectron spectroscopy (XPS) is then applied to detect the variation of elemental composition and functional groups. Fig. 5a shows the survey XPS spectra of composites before and after reduction in NaOH, and high resolution XPS spectra of C 1s core-level (Fig. 5b) and Fe 2p core-level (Fig. 5c). The binding energy is calibrated using C 1s peak at 284.6 eV. High peaks around

![Fig. 4. Raman spectra of GO and GO/Fe$_2$O$_3$ composites before and after reduction in 1 M NaOH.](image-url)

![Fig. 5. (a) The survey XPS spectra of composites before and after reduction in NaOH, and high resolution XPS spectra of (b) C 1s core-level and (c) Fe 2p core-level.](image-url)
285 eV and 533 eV can be clearly observed in Fig. 5a, corresponding to the C 1s and O 1s. The ratio of C/O is 2.86 and 7.33, before and after electrochemical reduction for composites respectively. The higher C/O ratio after electrochemical process indicates GO can be reduced efficiently. Two main peaks in the C1s spectra of the composite before reduction appear at 284.6 eV and 286.8 eV, as shown in Fig. 5b, corresponding to the sp²-hybridized graphitic carbon (C—C=C) in the basal plane and carbon atoms in C—O bonds [42]. The broad peaks in Fig. 5b in the range from 288 eV to 290 eV represent the carbon atoms in carboxyl (C=O/O—C=O) [43]. After reduction in NaOH, the intensity of the peak at 286.8 eV for C 1s spectra is much lower than the corresponding peak for composites before reduction, meaning that the relative content of functional groups containing C—O bonds decreases a lot after reduction. It demonstrates that the electrochemical reduction of GO mainly results from the reduction of C—O bonds.

Fig. 5c shows the XPS spectra of the Fe 2p core-level for GO/Fe2O3 composites, before and after electrochemical reduction. Binding energies of Fe 2p3/2 and Fe 2p1/2 are 711 eV and 724.5 eV respectively for GO/Fe2O3 composites before electrochemical reduction, in good agreement with crystalline Fe2O3. Also, the characteristic satellite peak of Fe2O3 at 719 eV appears before and after electrochemical reduction, further suggesting that the iron oxides before reduction is Fe2O3 [44]. Two other peaks at 710.2 eV and 723.5 eV appear for the ecrGO/FeOx composites, indicating the existence of Fe2+ for the composites after electrochemical reduction [45,46]. In the meantime, the satellite peak at 719 eV still appears in the composites after reduction. It may be because Fe2+ and Fe3+ coexist, and new structures of iron oxides/hydroxides rather than Fe2O3 might form during the cyclic voltammetry (CV) cycles between −1.2 V to 0 V. The reduction from Fe3+ to Fe2+ may result from cation intercalation [23] (such as H⁺ or Na⁺ in electrolyte).

3.3. Electrochemical performance of ecrGO/FeOx composites as binder-free electrodes

To evaluate the capacitive performance of ecrGO/FeOx composites (working potential ranging from −1.2 V to 0 V vs. Ag/AgCl), cyclic voltammetry (CV), EIS and galvanostatic charge/discharge are applied in a three-electrode system. The rate-dependent CV curves of the ecrGO and ecrGO/FeOx composites were measured in 1 M NaOH with the working potential window between −1.2 V and 0 V. Fig. 6a and b show the CV curves of the ecrGO and ecrGO/FeOx composites for different scan rates. The CV curves of ecrGO (Fig. 6b) under scan rates ranging from 10 mV s⁻¹ to 400 mV s⁻¹ display a quasi-rectangular shape with little distortion, indicating that ecrGO behaves almost as an ideal double-layer capacitor. The ecrGO/FeOx composite can basically exhibit a stable capacitive behavior when the scan rates increase, while the slight distortion of its CV curves when the scan rate increases to 400 mV s⁻¹ (Fig. 6a), is mainly attributed to the poor conductivity of FeOx. Hence the loss of capacity for composites under higher scan rates may result from the weaker conductivity of the composite than the ecrGO. Besides, a pair of redox peaks of the ecrGO/FeOx composites appears around −0.7 V and −1.12 V when scan rate is 10 mV s⁻¹, with the anodic peaks shifting positively and the cathodic peaks shifting negatively with the increasing scanning rates, as shown in Fig. 6a. This shift may be caused by the electrochemical polarization of the reversible reaction between Fe³⁺/Fe²⁺. So the working potential window for galvanostatic tests of charge and discharge ranges from −1.12 V to 0 V to avoid the hydrogen emission during charge and discharge. When the scan rates become faster, the electrochemical reaction is unable to keep the pace with the electron transfer due to the high charge transfer resistance (Rct), resulting in the anodic or cathodic peak being more positive or negative. This also may be the reason why the CV curves of the composites are slightly distorted under higher scan rates. The large Rct of the ecrGO/FeOx composites is further illustrated by the EIS results.

Additionally, Fig. 6c shows the specific capacitance of the ecrGO/FeOx composites and ecrGO, under various scan rates. The specific capacitance (Ccap) of the ecrGO/FeOx composites decreases from ~235 F g⁻¹ to 74 F g⁻¹ when the scan rate increases from 10 mV s⁻¹ to 400 mV s⁻¹, while there is a very small reduction for the Ccap of ecrGO (from ~76 F g⁻¹ to ~54 F g⁻¹). Although the ecrGO/FeOx composites show higher specific capacitance (Ccap) than ecrGO under different scan rates, the Ccap of ecrGO/FeOx composites drops faster than ecrGO with increasing scan rates. The distortion of the CV curves and the capacitive loss at high scan rates of the ecrGO/FeOx composites is further illustrated by the EIS results.
FeOx composites, when compared with ecrGO, may be caused by the lower conductivity and high $R_t$, of iron oxides. Therefore, although the specific capacitance of composites can be enhanced by introducing iron oxides into ecrGO, it does not mean that iron oxides in composites always benefit the capacitive performance, especially at high rates of charge and discharge.

The energy densities and power densities calculated are shown in Fig. 7, using the following equations [14]

\[
\text{Energy density} = \frac{1}{2} \times C_{sp} \times \Delta U^2
\]

\[
\text{Power density} = \frac{\text{Energy density}}{t_{\text{discharge}}}
\]

where $C_{sp}$ is the specific capacitance of electrodes ($\text{F g}^{-1}$), $\Delta U$ is the potential window (V), the unit for energy density is Wh kg$^{-1}$, $t_{\text{discharge}}$ is the time of discharge (hour), and the unit for power density is W kg$^{-1}$. The energy densities of ecrGO/FeOx composites are 47, 30, 25, 19, 15 Wh kg$^{-1}$ at power densities 1.41, 4.5, 7.5, 11.4, and 18 kW kg$^{-1}$, respectively. The energy densities of ecrGO/FeOx composite are higher than that of ecrGO at the same power densities.

To further compare and understand the electrochemical kinetics of ecrGO/FeOx composites and ecrGO for supercapacitors, electrochemical impedance spectroscopy (EIS) measurements were conducted from 100 kHz to 0.1 Hz, with an AC amplitude of 5 mV at open circuit potential. Fig. 8a shows typical Nyquist plots of the ecrGO/FeOx composites and ecrGO, including semi-circles in the high-frequency range (Fig. 8a) and straight lines in the low-frequency range (the insert in Fig. 8a). The semi-circle in the high-frequency range corresponds to the charge transfer resistance relating to the Faradic process [47]. A portion of the straight line with slope nearly 45° at the mid-frequency, as shown the insert in Fig. 8a (the magnification of Nyquist plot in the high-frequency region and the mid-frequency region), indicates the electrochemical behavior is controlled by the diffusion process [8]. In the low-frequency range, the more vertical lines, representing a rapid ion diffusion in the electrolyte and ion adsorption onto the surface of materials, suggests a more ideal capacitive performance of the electrodes [48]. The larger semi-circle of ecrGO/FeOx composites compared to that of ecrGO means a higher $R_t$, and can be attributed to the Faradic process between Fe$^{2+}$ and Fe$^{3+}$. The higher $R_t$ of ecrGO/FeOx composites than ecrGO also can provide an explanation that the CV curve is more likely to be distorted (Fig. 6a). The more vertical straight line in the low-frequency region of ecrGO compared to the ecrGO/FeOx composite indicates the more ideal capacitive performance of ecrGO. This is due to the less Faradic effect generated from Fe$^{2+}$/Fe$^{3+}$ for ecrGO, thus ecrGO more likely acts as a double-layer capacitor than ecrGO/FeOx.

An equivalent circuit model for fitting EIS data is shown in Fig. 8b. The high-frequency intercept with real axis and semi-circle correspond to the electrolyte resistance ($R_s$) and the charge transfer resistance ($R_t$), respectively. The portion of the straight line with slope nearly 45° at the mid-frequency represents the Warburg resistance ($W_a$) of ionic diffusion from electrolyte to the surface of electrode, in series with $R_t$. The Warburg element is selected due to the frequency dependence of porous materials and counter ion diffusion to electrode surface during Faradic process [49]. Constant phase elements (CPE$_1$), in parallel with $R_s$ and $W_a$, is used to model the semicircle in high frequency. And CPE$_2$ is applied to describe the nearly linear line in low frequency [14]. From the model, the $R_t$ values for ecrGO and the ecrGO/FeOx composite are 6.6 $\Omega$ and 19.5 $\Omega$, respectively. The higher $R_t$ of the ecrGO/FeOx composite than that of the ecrGO mainly results from Faradic process between Fe$^{2+}$ and Fe$^{3+}$. The Warburg resistance of the ecrGO/FeOx composite is 26 $\Omega$ and Warburg resistance of the ecrGO is 28.8 $\Omega$. The smaller Warburg resistance of the ecrGO/FeOx composite means the more effective diffusion process from electrolyte to electrode surface, when compared with ecrGO. The better ionic diffusion process for the ecrGO/FeOx composite may be attributed to intercalation of iron oxide particles between ecrGO sheets, facilitating ionic diffusion to the surface of ecrGO/FeOx composites.
Fig. 8c represents the imaginary part of the capacitance \( (\text{C}^*) \) as a functional of frequency. The imaginary part of capacitance corresponds to the energy dissipation of the capacitor and is a characteristic of an irreversible process, which can result in the hysteresis of the electrochemical process [50,51]. The \( \text{C}^* \) goes through the maximum value at a frequency known as the relaxation frequency \( f_r \), so the characteristic time constant \( \tau_0 \) can be determined according to the equation \( \tau_0 = (2\pi f_r)^{-1} \) [51]. \( \tau_0 \) is the minimum time required to discharge all the energy with an efficiency more than 50% of its maximum value [52,53]. The constant times of 0.19 s and 0.4 s are obtained for ecrGO and ecrGO/FeO\(_x\) composites respectively, meaning a faster discharging time of the ecrGO than that of the ecrGO/Fe\(_2\)O\(_3\) composites. It may be due to the less faradic effect in ecrGO than the ecrGO/FeO\(_x\) composite.

The galvanostatic charge and discharge of ecrGO/FeO\(_x\) composites and ecrGO in long-term cycle was carried out under various constant current densities (1 A g\(^{-1}\), 2 A g\(^{-1}\), 4 A g\(^{-1}\)) to detect the stability. The specific capacity of electrodes can be obtained at different constant current densities according to the equation below:

\[
C_{sp} = \frac{1}{\Delta t} \frac{I}{m} (V_f - V_i)
\]

Where \( I/m \) (A g\(^{-1}\)) is the constant current density for charge and discharge, \( \Delta t \) (s) is the time duration for discharging, \( V_f \) (V) and \( V_i \) (V) are the initial and final potentials for discharge respectively. All the charge/discharge curves under different current densities have a triangular shape with little distortion, as shown in Fig. 9 inserts, suggesting the ecrGO/FeO\(_x\) composites and ecrGO exhibit capacitive behavior. For charge and discharge curves of ecrGO/FeO\(_x\) composites shown in Fig. 9a, the platforms of charging and discharging can be observed at \(-1.1\) V and \(-0.7\) V at a current density of 1 A g\(^{-1}\), correspondingly. This charging/discharging platform is contributed from the reversible reaction between Fe\(^{2+}\) and Fe\(^{3+}\), in agreement with the CV results in Fig. 2a. When the current density increases to 2 A g\(^{-1}\), the duration of the charging/ discharging platform shorten. This platform is barely observed when the current density further increases to 4 A g\(^{-1}\). It can be attributed to the more severe polarization resulted from the internal resistance and charge transfer resistance when higher current passed through the electrodes. For charge and discharge curves of ecrGO shown in Fig. 9b insert, platforms are hardly observed, attributing to the little redox reaction on ecrGO.

The specific capacity of ecrGO/FeO\(_x\) composites and ecrGO for 2000 cycles of charge and discharge were measured, as shown in Fig. 9. For ecrGO/FeO\(_x\) composite shown in Fig. 9a, a \( C_{sp} \) value of 195 F g\(^{-1}\) can be obtained at a current density of 1 A g\(^{-1}\) after 500 cycles, and its \( C_{sp} \) of 176 F g\(^{-1}\) (\(-10\%) \) drop at 2 A g\(^{-1}\) and 160 F g\(^{-1}\) (\(-18\%) \) drop at 4 A g\(^{-1}\) are obtained, when cycle number goes to the 1000 and 1500, respectively. The measured \( C_{sp} \) is 181 F g\(^{-1}\) at the 2000th cycle, when the current density returns to 1 A g\(^{-1}\) and a retention of 92% can be obtained after 2000 cycles of charging and discharging, indicating good electrochemical stability for the ecrGO/FeO\(_x\) composite. The small decrease of \( C_{sp} \) for the composites may be due to the fading of FeO\(_x\) during the long life cycle of charge and discharge. As shown in Fig. 9b, the calculated \( C_{sp} \) of ecrGO is 80 F g\(^{-1}\), 73 F g\(^{-1}\) and 66 F g\(^{-1}\) under current density of 1 A g\(^{-1}\), 2 A g\(^{-1}\), and 4 A g\(^{-1}\), respectively. The \( C_{sp} \) value of 75 F g\(^{-1}\) can be obtained when current density turns back to 1 A g\(^{-1}\). The retention for ecrGO after 2000 cycles of charge and discharge is 93.7%, slightly higher than that of ecrGO/FeO\(_x\) composites.

Table 1 shows the comparison of the specific capacitance of rGO/iron oxides among the reported works and this work. The capacitive performance of rGO/iron oxides composites varies maybe because of the different structures of iron oxides, the treatment of reduced GO, different current collectors and various testing methods. The specific capacitance of ecrGO/iron oxides composites in this work shows the relative high value, although it is not the best one among those reported works. Here, this work mainly presents a facile strategy for fabricating reduced GO/iron oxides composites, as binder-free electrodes for supercapacitors, via electrochemical process. Also the study illustrates the synergistic effect between ecrGO and iron oxides during the electrochemical process. The relative high \( C_{sp} \) of ecrGO/iron oxides composites in potential range from \(-1.2\) V to 0 V indicates it can be a promising candidate as an anode when fabricating an asymmetric supercapacitor.

4. Conclusions

Sandwich-like composites of electrochemical reduced GO and iron oxides with relative high specific capacitance and retention were developed for supercapacitors. A facile electrochemical reduction approach was applied to reduce GO to ecrGO in an alkaline solution, after electrochemical reduction the ecrGO/FeO\(_x\) composite can be directly used as electrodes without any binders. This sandwich-like ecrGO/FeO\(_x\) composite exhibits a high \( C_{sp} \) (195 F g\(^{-1}\) at 1 A g\(^{-1}\), 235 F g\(^{-1}\) at a scan rate of 10 mV s\(^{-1}\)) and good cycling stability (92% retention after 2000 charging/discharging cycles) because of the synergistic effect between ecrGO and iron oxides in ecrGO/FeO\(_x\) composites. The ecrGO can act as a framework for anchoring the iron oxides, which in turn can introduce pseudocapacitance to the composites and hinder the
stacking of the ecrGO sheets. Also, the composites have a good mechanical strength, as indicated in the SEM and Raman results. The ecrGO/FeOx composite possesses much higher Csp than ecrGO due to the pseudocapacitance of the iron oxides, although the Csp of the ecrGO/FeOx composites decreases with the increasing discharge rates because of the high Rct and poor conductivity of the iron oxides. Hence, iron oxides in composites do not always benefit the capacitive performance, especially at high rates of charge and discharge. The optimal combination of ecrGO and iron oxides needs to be studied further. The ecrGO/FeOx composite reported here is still a good candidate for supercapacitors. This composite as a binder-free anode for an asymmetric supercapacitor will be fabricated and investigated in our following research.

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Appendix A. Supplementary data

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References


