Enhanced electrochemical performances of FeO\textsubscript{x}/graphene nanocomposites as anode materials for alkaline nickel-iron battery

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A new type of graphene-based FeO\textsubscript{x} nanocomposites has been synthesized by high temperature solid-state reaction using FeC\textsubscript{2}O\textsubscript{4}•2H\textsubscript{2}O. The synthesis conditions are optimized by thermogravimetric analysis of the precursor. When evaluated as anode material for alkaline nickel-iron battery, the FeO\textsubscript{x}/graphene nanocomposites deliver a high specific capacity of 552.1 mAh g\textsuperscript{-1} at current density of 200 mA g\textsuperscript{-1} and remain 91\% of the initial capacity after 100 cycles. Furthermore, the hybridized FeO\textsubscript{x}/graphene materials only provide 26\% capacity decay when the discharge current density converts from 200 mA g\textsuperscript{-1} to 1000 mA g\textsuperscript{-1}. The enhanced cycling and high-rate performance is owing to the high specific surface area of iron oxide nanoparticles and particular electric conductivity of graphene. This study suggests a safe, inexpensive and powerful rechargeable iron electrode, enabling the promising prospect of large-scale energy storage based on the aqueous iron-based rechargeable battery.

1. Introduction

Rechargeable batteries are extraordinary suitable for large-scale storage of electrical energy based on their high energy efficiency and scalability\textsuperscript{1,2}. As an example, Lithium ion battery, lead-acid battery and nickel-metal hydride (Ni-MH) battery have played major roles in various application fields, respectively. Meanwhile, the relatively low cost, eco-friendliness as well as the further safety requirements for rechargeable batteries have also attracted increasingly attention. The unreliable safety of lithium ion battery lies in the organic electrolytes and the high activity of Li containing in electrode materials\textsuperscript{3,4} has been questioned by most of the researchers. More than that, the toxicity of lead-acid battery and the high cost limitation of Ni-MH battery are seemly irreversible. Consequently, searching for promising alternatives which could be applied with inexpensive materials in relatively safe aqueous electrolytes is extremely urgent.

Developed around 1900s by Waldemar Jungner and Thomas Edison, nickel-iron battery used to be widely discussed for large-scale energy storage\textsuperscript{5-9}. With Ni(OH)\textsubscript{2} as the cathode and iron as the anode, the century-old Ni-Fe battery was considered to be one of the most promising secondary batteries for a long time\textsuperscript{10}. Nowadays, the Ni-Fe energy storage systems have been widely employed into the electricity grid owing to their low cost, durable in use, eco-friendliness and safety. Nevertheless, the high self-discharge\textsuperscript{11,12}, relative low energy efficiency\textsuperscript{11,12}, especially the low power density\textsuperscript{13} of the iron anode in aqueous alkaline media are the principal drawbacks seriously restricting further utilization of iron battery. Because of the passivation\textsuperscript{14,15} onto the surface of iron electrode, the practical capacity only achieves as low as nearly 1/3 of the theoretical value (962 mAh g\textsuperscript{-1}). Seriously, the formation of passive layer also leads to the bad performance in high-rate discharge. It is worthwhile to significantly improve the electrochemical performances of iron electrode at high discharge rate, aimed at applications in hybrid electric vehicles (HEV) and electric vehicles (EV) where high current response is needed.

Graphene-based composites have been intensively explored in a wide range of applications\textsuperscript{16,17}, including supercapacitors\textsuperscript{18}, fuel cells\textsuperscript{19}, photovoltaic devices\textsuperscript{20}, photocatalysis\textsuperscript{21}, batteries\textsuperscript{22-26}, and so on. In the previous study, Wang\textsuperscript{27} reported a strongly coupled FeO\textsubscript{x}/graphene hybrid as anode for ultrafast nickel-iron battery, they successfully increased the charging and discharging rates by nearly 1000-fold over traditional Ni-Fe batteries. In this work, a novel hybridized FeO\textsubscript{x}/graphene anode material was prepared through a relatively simple high temperature solid-state reaction process instead of hydrothermal synthesis. The iron oxide particles recrystallized on the reduced graphene sheets during high temperature decomposition process. Obviously, direct growth of iron nanoparticles on graphene sheets provided a good contact between the FeO\textsubscript{x} nanoparticle and the two-dimensional network of graphene, thus realized efficient conduction of charge carriers and enhances the structural stability. Consequently, the FeO\textsubscript{x}/graphene composites can afford excellent electrochemical performances at high discharge current density.
2. Experimental Section

2.1 Synthesis of the hybridized FeOx/graphene materials

Graphene oxide (GO) was made by a modified Hummers method using graphite powder (200 mesh, 99.9999%, Sigma-Aldrich). The FeOx/graphene hybrids were synthesized by a ball milling method followed by high temperature solid-state reaction process. Ferrous oxalate dihydrate (99.99%, Sigma-Aldrich) (FOD) and the as-prepared GO (10 mg/mL) were mixed based on the mass ratio ($m_{\text{FOD}}:m_{\text{GO}} = 100:1.0, 100:1.5$ and $100:2.0$), and 5% glucose was added to provide the reducing agent, and ethanol (5 mL) was used as the dispersing agent. Then the raw materials were ball-milled respectively under Ar atmosphere using a spex800 ball mill machine for 6 h with the ball-to-powder weight of 10:1. The intermediate products were kept at 80°C for 12 h to intensive drying under vacuum. After that, the obtained precursors were heated at 350°C for 0.5 h, then, 400°C for 6 h, and finally, calcinated at 700°C for 16 h under argon atmosphere to produce the final FeOx/graphene composites. For comparison, FeOx composites were also prepared by a similar procedure in the absence of GO.

2.2 Characterization

Thermogravimetric analysis of the FeOx/graphene precursor was investigated using a TG/DSC (SDT-2960, USA) apparatus with a temperature range from 100°C to 700°C (10°C min⁻¹) under argon atmosphere. Furthermore, the composition and phase purity of the as-prepared samples were characterized by X-ray diffraction (XRD) (D8 Focus, Bruker, Germany). SEM images were carried out on an S-4800 (Hitachi, Japan) scanning electron microscopy (SEM). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were carried out on a Hitachi-600 transmission electron microscope at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurement was performed on a ESCALAB MK II XPS Spectrometer to analyze the surface composition, using monochromated Al Kα X-rays. Cyclic voltammetry (CV) measurements were performed using a VMP3 Electrochemical Workstation (Bio-logic Inc.) in the range of -0.4 V to -1.4 V on a three-electrode configuration, where a mercury/mercuric oxide (MMO) was used as the reference electrode ($E^0 = +0.098$ V vs. the normal hydrogen electrode), and nickel hydroxide as the counter electrode. Particularly, the electrolyte was 8 M KOH and 1 M LiOH mixed aqueous solution.

2.3 Preparation of working electrodes and electrochemical measurements

The anode electrode typically contained 92 wt% of the synthesized FeOx/graphene materials, 5 wt% of bismuth oxide, and 3 wt% of hydroxypropyl methyl cellulose (HPMC). After the mixture was dispersed in D.I. water, the pastes were then loaded onto a circular Ni foam current collectors ($r = 8$ mm, 110 ppi). The substrates were dried at 80°C for 6 h in vacuum and then compressed to 0.5 mm thickness before measurement. Subsequently, the working electrodes were tested in a miniature cell, using two sintered nickel electrodes as cathode to achieve excess capacity and no-woven PP cloth as separator. According to the related references, we chose 8 M KOH aqueous solution including 1 M LiOH as the electrolyte. Finally, the electrochemical measurements were carried out by a LAND battery-test instrument (Wuhan, China) at room temperature. The specific capacity and cycle life at different current densities were tested to evaluate the performance of the hybridized materials.

3. Results and discussion

TG-DSC analysis (Fig. 1) of the ball-milled precursor was carried out to investigate the solid-phase reaction process of FeOx/graphene precursor within the temperature range 100°C to 700°C at a rate of 10°C min⁻¹. The results indicate three significant weight loss regions. The first region (150-200°C) is related to the dehydration of the hydrates. The second platform of weak weight loss is observed at approximate 330°C, corresponding to the GO reduction process based on the weight loss ratio. Subsequently, the thermal decomposition of FeC₂O₄ causes the endothermic peak at nearly 400°C followed with the glucose carbonization at above 500°C.

![Fig. 1 TG-DSC curve of the FeOx/graphene ($m_{\text{FOD}}:m_{\text{GO}} = 100:1.5$) precursor.](image)

![Fig. 2 XRD patterns of FeOx/graphene composites based on different weight ratios of FOD and GO.](image)
Fig. 2 shows the XRD patterns of the FeO\(_x\) composites based on the weight ratios of FOD and GO. The narrow sharp peaks indicate the good crystallization of the samples. It is noteworthy that the FeO\(_x\) grown on the reduced GO sheet was a mixture of Fe\(_2\)O\(_3\) and FeO. Particularly, for the sample (m\(_{\text{FOD}}\):m\(_{\text{GO}}\) = 100:2), it is obviously noted that no FeO peaks can be detected in the product, indicating that the content of FeO particles decreased with the increase of GO. It can be supposed that the FeO particles were further oxidated by the redundant water and the oxidizing agent produced along with the reduction process of GO. To make a brief conclusion, the decomposition process of the FeC\(_2\)O\(_4\)•2H\(_2\)O can be expressed as:

\[
\text{FeC}_2\text{O}_4\cdot2\text{H}_2\text{O} \xrightarrow{\text{decomposition}} \text{FeO}+\text{Fe}_2\text{O}_3+\text{CO}+\text{H}_2\text{O} \quad (1)
\]

To further investigate the chemical structure of the iron particles, typical XPS analysis was evaluated and the results are shown in Fig. 3. In the XPS Fe 2p spectrum (Fig. 3a), two peaks at 711.1 eV and 724.5 eV are detected, which are assigned to Fe 2p\(_{3/2}\) and Fe 2p\(_{1/2}\) binding energies. The Fe 2p\(_{3/2}\) electron-binding energy observed in Fig. 3a reveals that the compound FeO\(_x\) contains a majority of Fe\(_2\)O\(_3\). FeO was barely detected in the XPS spectrum possibly owing to the trace content and graphene covering. The deconvoluted O 1s XPS spectrum (Fig. 3b) shows two peaks at 530.1 eV and 531.9 eV, indicating the presence of O\(^2\) and OH\(^-\), respectively. These results obviously indicate that the iron particles exist in a mixed state of iron oxides and a small amount of intermediate product FeOOH, produced during the FeC\(_2\)O\(_4\)•2H\(_2\)O pyrolysis. The characteristic peak of graphene at 284.8 eV is shown in detail in the XPS C 1s spectrum (Fig. 3c), which confirmed the existence of reduced graphene oxide (rGO). The high temperature reaction process of FeO\(_x\) recrystallization and graphene oxide reduction contributes to the intensive mixing between iron oxides and graphene.

Fig. 4 Raman spectra of graphene oxide and FeO\(_x\)/graphene composites based on different weight ratios of FOD and GO.

Raman spectroscopy is widely used to evaluate the reduction degree of GO. The spectra of graphene oxide and FeO\(_x\)/graphene composites are plotted in Fig. 4. Characteristic peaks of FeO\(_x\)/graphene materials at around 1340 cm\(^{-1}\) (D band) and around 1590 cm\(^{-1}\) (G band) are detected. The intensity ratio of D and G peak (I\(_D\)/I\(_G\)) reveals the disorder density of carbon materials. As shown in Fig. 4, compared with the GO (I\(_D\)/I\(_G\) = 0.86), the I\(_D\)/I\(_G\) of FeO\(_x\)/graphene is increased to nearly 1.10 due to the removal of oxygen-containing functional groups during the progress of GO reduction. The analysis of Raman spectra indicate that GO in the composite is reduced sufficiently.
SEM image of the FeO\(_x\)/graphene (m\(_{\text{FeOx}}\):m\(_{\text{GO}}\) = 100:1.5) composites (Fig. 5a) reveals that the FeO\(_x\) nanoparticles coat on the graphene sheet evenly. Most of the nanoparticles are sphere shape with the diameters ranging from 20 to 100 nm, compared with the blank sample (Fig. 5b), which are in the size range of 1-3 \(\mu\)m, and strongly aggregate together. It is because that direct growth of inorganic nanomaterials on mildly oxidized nanocarbon materials affords strong covalent coupling between inorganic nanocrystals and carbon materials, which impedes the nanoparticles from crystallization. In Fig. 5c, the TEM image clearly shows the nanoparticle grown on the GE sheets. The HRTEM image of the FeO\(_x\)/graphene composites shown in Fig. 5d reveals the lattice spacing of 0.47 nm corresponding to the (111) plane of Fe\(_3\)O\(_4\) which deeply proves the existence of Fe\(_3\)O\(_4\) in the FeO\(_x\) composites.

![Image](https://example.com/fig5.png)

**Fig. 5** SEM images of the FeO\(_x\)/graphene composites, (a) m\(_{\text{FeOx}}\):m\(_{\text{GO}}\) = 100:1.5 (b) m\(_{\text{FeOx}}\):m\(_{\text{GO}}\) = 100:0; (c) TEM and (d) HRTEM images of the FeO\(_x\)/graphene (m\(_{\text{FeOx}}\):m\(_{\text{GO}}\) = 100:1.5).

Cyclic voltammograms (CVs) have been performed to investigate the oxidation-reduction behavior of FeO\(_x\)/graphene system. Fig. 6a shows the CV curves of the different FeO\(_x\) electrodes. The FeO\(_x\)/graphene (m\(_{\text{FeOx}}\):m\(_{\text{GO}}\) = 100:1.5) sample performs a better reversible electrochemical oxidation-reduction process, relatively. Even at larger scan rates (Fig. 6b), the strong oxidation and reduction peaks are still observed implying the excellent reversibility of the hybrid materials at high current density. According to the previous study\(^{31, 32}\), multiple peaks should be observed in the CV curves on the behalf of redox reaction of iron electrode. But, in particular, the CV curve only emerges one overlapping redox peak at -1.08 V, mainly involving with the conversion between Fe\(^{3+}\) to Fe. Two obvious oxidation peaks at -0.87 V and -0.55 V, emerging higher potential and stronger intensity. Respectively, the two oxidation peaks represent Fe/Fe\(^{2+}\) and Fe\(^{3+}/Fe^{4+}\) which can be indicated by the following reactions:\(^{32}\):

\[
\begin{align*}
\text{Fe} + 2\text{OH}^- \overset{\text{charge}}{\underset{\text{discharge}}{\rightarrow}} \text{Fe(OH)}_2 + 2\text{e}^- & \quad E^0 = -0.877 V \quad (2) \\
\text{Fe(OH)}_2 + \text{OH}^- \overset{\text{charge}}{\underset{\text{discharge}}{\rightarrow}} \text{FeOOH} + \text{H}_2\text{O} + \text{e}^- & \quad E^0 = -0.560 V \quad (3)
\end{align*}
\]

In order to investigate the specific capacity of the FeO\(_x\)/graphene composites, the charge-discharge cycles at a discharge current density of 200 mA g\(^{-1}\) were carried out. As shown in Fig. 6c, two discharge plateaus are observed in discharge process, which can be attributed to the reaction of Fe\(^{3+}\)→Fe\(^{2+}\) and Fe\(^{2+}\)→Fe\(^0\), respectively. Obviously, the discharge capacities of FeO\(_x\)/graphene composites are more than twice as much as the blank sample. Especially for the samples (m\(_{\text{FeOx}}\):m\(_{\text{GO}}\) = 100:1.5), the maximum discharge capacity can maintain at 552.1 mAh g\(^{-1}\) (compared with 222.6 mAh g\(^{-1}\) of the FeO\(_x\) material without graphene). The electrochemical performance of the FeO\(_x\)/graphene hybrids is further evaluated by high-rate discharge measurement. Fig. 6d shows the discharge capacity of the FeO\(_x\)/graphene hybrids at different current densities from 100 mA g\(^{-1}\) to 1000 mA g\(^{-1}\). As expected, our FeO\(_x\)/graphene composites express excellent high-rate performance. Especially for the optimal sample (m\(_{\text{FeOx}}\):m\(_{\text{GO}}\) = 100:1.5), the specific capacity converted from 549.4 mAh g\(^{-1}\) to 408.5 mAh g\(^{-1}\), based on the discharge current densities of 100 mA g\(^{-1}\) and 1000 mA g\(^{-1}\), respectively. The outstanding electrochemical performance can be attributed to the following reasons; first of all, the size of the FeO\(_x\) particles decrease to a large extent because of the strong coupling with graphene during decomposition-crystallization progress, which contributes to larger efficient surface area. Another important reason is that GE layers can enhance the electron transfer through the nano-sized active materials during charging and discharging.
method of synthesizing iron anode materials for improving the power density of rechargeable iron battery for large-scale energy storage, as well as electric vehicles and hybrid electric vehicles.

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Notes and references


Graphic Abstract
Graphical and textual abstract

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Highlight:

□ In this work, a novel hybridized FeOₓ/graphene material was prepared through a relatively simple high temperature solid-state reaction process instead of hydrothermal synthesis.

□ When evaluated as anode material for alkaline nickel-iron battery, the FeOₓ/graphene nanocomposites delivered a high specific capacity of 552.1 mAh g⁻¹ at current density of 200 mA g⁻¹ and remained 91% of the initial capacity after 100 cycles.

□ The FeOₓ/graphene composites can afford excellent electrochemical performances at high discharge current density (as high as 1000 mA g⁻¹), aimed at applications in hybrid electric vehicles (HEV) and electric vehicles (EV) where high current response is needed.