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A Facile Electrophoretic Deposition Route to the Fe₃O₄/CNTs/rGO Composite Electrode as a Binder-Free Anode for Lithium Ion Battery

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Supporting Information

ABSTRACT: Fe₃O₄ is regarded as an attractive anode material for lithium ion batteries (LIBs) due to its high theoretical capacity, natural abundance, and low cost. However, the poor cyclic performance resulting from the low conductivity and huge volume change during cycling impedes its application. Here we have developed a facile electrophoretic deposition route to fabricate the Fe₃O₄/CNTs (carbon nanotubes)/rGO (reduced graphene oxide) composite electrode, simultaneously achieving material synthesis and electrode assembling. Even without binders, the adhesion and mechanical firmness of the electrode are strong enough to be used for LIB anode. In this specific structure, Fe₃O₄ nanoparticles (NPs) interconnected by CNTs are sandwiched by rGO layers to form a robust network with good conductivity. The resulting Fe₃O₄/CNTs/rGO composite electrode exhibits much improved electrochemical performance (high reversible capacity of



540 mAh g^{-1} at a very high current density of 10 A g^{-1} , and a remarkable capacity of 1080 mAh g^{-1} can be maintained after 450 cycles at 1 A g^{-1}) compared with that of commercial Fe₃O₄ NPs electrode. KEYWORDS: Fe_3O_4 , carbon nanotubes, reduced graphene oxide, lithium ion battery, anode, electrophoretic deposition

1. INTRODUCTION

Since commercial lithium ion batteries (LIBs) were developed by Sony Corporation Japan in June 1991,¹ LIBs with long lifespan and light weight due to their high energy density have been the dominant power supply in portable electronic devices.^{2,3} Although LIBs are superior to other battery technologies in terms of energy density, present LIBs have not yet met the demand of the emerging applications, such as electric (EV) and hybrid (HEV) vehicles.⁴ The commercial graphite anode used currently has already reached its theoretical limit (372 mAh g^{-1}), and it is a major barrier to develop high energy/power density LIBs for EV and HEV.⁵ Thus, exploring alternative anode materials with higher specific capacities has become an urgent task nowadays.⁶

Transition metal oxides are considered promising candidates for high energy density LIBs owing to their higher specific capacity, usually several times higher than that of graphite. Among them, magnetite (Fe_3O_4) has been extensively studied because of its natural abundance, eco-friendliness, and low cost.^{7,8} Despite the above predominant advantages of Fe_2O_4 , its low electronic conductivity and huge volume changes upon Li⁺ ions insertion and extraction result in dramatic pulverization and loss of electrical contact between active materials and the electrode framework, leading to rapid capacity fading during cycling.

Two typical strategies have been frequently put forward to overcome these obstacles. One method is to fabricate nanostructured Fe₃O₄, such as Fe₃O₄ nanocrystals,^{10,11} Fe₃O₄

nanospheres,⁹ Fe₃O₄ nanorods,^{12–14} Fe₃O₄ nanocages,¹⁵ Fe₃O₄ nanospindles,¹⁶ and Fe_3O_4 nanotubes.¹⁷ Nanostructured Fe_3O_4 materials can shorten the diffusion paths of Li⁺ ions, leading to higher ionic conductivity.¹⁸ Another feasible route is to introduce carbon materials such as carbon nanotubes (CNTs) and graphene.¹⁹⁻²² It has been proved that CNTs and graphene can not only enhance the electronic conductivity of the electrode but also provide buffer spaces to accommodate the strains during lithiation/delithiation process, leading to improved structural and electrical integrity of Fe₃O₄ anodes.^{23,24} Despite the enhanced electrochemical performance that has been achieved in the above successful demonstrations, the material synthesis and electrode fabricating processes are usually separate. For fabrication of the electrode, the conventional method is coating the slurry containing nanostructured active materials, conductive agents, and binders to the current collector. The indispensable binders do not contribute to the actual battery capacity and easily cause aggregation of nanosized active materials.^{25,26}

Here, we introduce a new electrode design concept that both the material synthesis and electrode fabricating processes can be simultaneously achieved and that no binders are needed. Fe_2O_3 nanoparticles (NPs), CNTs, and graphene oxide (GO) are assembled to Fe₂O₃/CNTs/GO composite electrode by the

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Figure 1. Schematic fabrication process for the Fe₃O₄/CNTs/rGO composite electrode.

electrophoretic deposition (EPD) method (Figure 1). After subsequent heat treatment, the final $Fe_3O_4/CNTs/rGO$ composite electrode is obtained. In this characteristic structure, Fe_3O_4 NPs are tethered by CNTs and sandwiched by graphene sheets to form a robust network. Owing to the synergetic effects of CNTs and flexible graphene, this composite electrode can not only provide high electronic conductivity but also restrain volume changes during cycling. Commercial Fe_3O_4 NPs electrode is also prepared by the conventional slurry coating method. Compared to it, the $Fe_3O_4/CNTs/rGO$ composite electrode exhibits much improved electrochemical performance due to the specific structure.

2. EXPERIMENTAL SECTION

2.1. Materials. CNTs suspension in *N*-methyl-2-pyrrolidone (wt % = 8%, Chengdu Organic Chemicals Co., Ltd.), GO powder (Shanghai Ashine Technology Development Co., Ltd.), I₂ (Aladdin), acetone (Xilong Chemical Co., Ltd.), and commercial Fe₃O₄ NPs (Alfa Aesar, 20–30 nm APS powder, specific area = $60 \text{ m}^2 \text{ g}^{-1}$, SEM images are shown in Figure S1) were used without further purification. The starting material Fe₂O₃ NPs were synthesized according to a hydrothermal method.⁴ Typically, 0.26 g (1.6 mmol) of FeCl₃ (Sinopharm Chemical Reagent Co., Ltd.) and 0.07 g (0.4 mmol) of L-arginine (Aladdin) were first dissolved in 80 mL of distilled water and stirred for 1 h to form a clear yellow solution. Subsequently, the solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was sealed and heated at 150 °C for 12 h and then cooled down to room temperature naturally. The red precipitate was collected by centrifugation, washed several times with deionized water, and freeze-dried.

2.2. Fabrication of the Fe₃O₄/CNTs/rGO Composite Electrode. In a typical experiment, 0.02 g of GO was dispersed in 10 mL of acetone by ultrasonication for 1 h. Then, 0.05 g of Fe₂O₃ NPs, 0.05g of I₂, 0.125 g of CNTs suspension, and 40 mL of acetone were then added into the GO suspension and further dispersed by using a homogenizer (T10 basic, IKA works GmbH & Co., Germany) for 1 h to obtain the EPD suspension. The EPD deposition was carried out under potentiostatic conditions, using a dc supply as shown in Figure 1. The deposition substrate (working electrode) was a 2 cm \times 3 cm piece of Cu foil (10 μ m thickness). The counter electrode was a 3 cm \times 4 cm piece of Pt plate (2 mm thickness). The two electrodes were anchored to a polytetrafluoroethylene (PTFE) electrode holder, respectively, and placed 1.5 cm apart. After applying a dc voltage of 100 V between these two electrodes for 15 s, the Fe₂O₃/CNTs/GO composite film deposited on the Cu foil could be obtained. The asprepared Fe₂O₃/CNTs/GO composite electrode was dried in a vacuum oven at 80 °C for 12 h and subsequently annealed at 700 °C for 4 h at the heating rate of 5 °C min⁻¹ under the Ar atmosphere to obtain the final $Fe_3 \check{O_4}/CNTs/rGO$ composite electrode. The loading mass of Fe₃O₄/CNTs/rGO composite on the Cu foil is about 0.71 mg cm^{-2} .

2.3. Characterization. The zeta potentials were measured on the zeta potential analyzer (90 Plus PALS, Brookhaven). The X-ray diffraction (XRD) data of samples were collected with the Rigaku miniflex 600 X-ray diffractometer, using Cu K α radiation from 10 to 70° at 2° min⁻¹ with the recording interval of 0.02°. Raman spectra

were acquired on the Xplora Raman microscopy system (Horiba) with 532 nm Ar-ion laser. XPS measurements were performed on PHI Quantum 2000. Thermogravimetric analysis (TGA) was taken on Netzsch TG 209 F1 under air flow ($35-900 \degree C$, $10 \degree C min^{-1}$). SEM and EDS mapping images were obtained by field-emission scanning electron microscopy (FESEM, HITACHI S-4800) equipped with an accessory of X-ray spectroscopy (energy dispersive spectrometer, EDS, OXFORD 7593-H). TEM images were recorded by using the high-resolution transmission electron microscopy (HRTEM, JEOL-2100) and (FEI, TECNAI G2 F30).

2.4. Electrochemical Measurements. The electrochemical measurements of these samples were performed using CR2016 coin cells assembled in an argon-filled glovebox. Lithium foil was used as the counter electrode. Celgard 2400 membrane was used as the separator. The solution of 1 M LiPF₆ in ethylene carbonate (EC)/ diethyl carbonate (DEC) (1:1, vol %) was used as the electrolyte. The Fe₂O₄/CNTs/rGO composite electrode was used as the working electrode, and the contrast samples of commercial Fe₃O₄ NPs electrode were also prepared by using the conventional slurry coating method. The mixture of Fe₃O₄ NPs, acetylene black, and polyvinylidene difluoride (PVDF), at a weight ratio of 70:20:10, was dispersed in N-methyl-2-pyrrolidone (NMP) to form a slurry. Then, the slurry was coated onto the Cu foil and subsequently dried in a vacuum oven at 80 °C for 12 h. The galvanostatically charge and discharge tests were carried out on the battery test system (NEWARE, Shenzhen, China) between 0.01 and 3.0 V. Electrochemical impedance spectra (EIS) were acquired on the electrochemical workstation of Solartron SI 1287 with frequencies range from 0.1 Hz to 100 kHz.

3. RESULT AND DISCUSSION

For a typical EPD process, charged particles suspended in a stable suspension, and their migration and deposition are driven by a dc electric field between two electrodes (Figure 1).^{27,28} Thus, the success of multicomponents EPD is dependent on the same ionic charge around each component in the EPD suspension.^{29,30} Unless each component have the same sign of charge, the deposition would not happen on the same electrode (cathode or anode). Zeta potentials (ξ) of Fe₂O₃, CNTs, and GO in acetone are examined. As shown in Table 1, Fe₂O₃ is negatively charged, but both CNTs and GO

Table 1. Comparison of Zeta Potentials of Fe_2O_3 , CNTs, and GO Suspended in Acetone before and after I_2 Is Added

samples	ξ (mV)	ξ (mV), 1 g $\rm L^{-1}~I_2$ is added
Fe_2O_3 (1 g L ⁻¹)	-39.51	38.53
CNTs $(0.2 \text{ g } \text{L}^{-1})$	45.10	58.69
GO $(0.4 \text{ g } \text{L}^{-1})$	14.85	61.88

are positively charged. Thus, it is impossible to carry out EPD on these components without pretreatment. In this case, addition of a suitable dispersant is necessary to make all components have the same sign of charge. I_2 is chosen as the dispersant, beacuse it can be easily removed during the drying process in the vacuum oven. It is reported that I_2 reacts with

acetone (eq 1), which creates protons; the adsorption of the generated protons onto the surface of the suspended particles will make them positively charged and enhance the electrostatic repulsion force to make the suspension more stable.^{29,31,32}

$$CH_3COCH_3 + 2I_2 \leftrightarrow ICH_2COCH_2I + 2I^- + 2H^+$$
(1)

As shown in Table 1, after I₂ is added, ξ of Fe₂O₃ transforms into 38.53 mV, and ξ of CNTs and GO increase to 58.69 and 61.88 mV. All positively charged components can be deposited on the cathode simulanteously when a appropriate voltage is applied.

Figure 2 shows the photographs of the $Fe_2O_3/CNTs/GO$ composite electrode obtained through EPD and $Fe_3O_4/CNTs/$



Figure 2. Photographs of (a) front and (b) side of the $Fe_2O_3/CNTs/GO$ composite electrode. Photographs of (c) front and (d) side of the $Fe_3O_4/CNTs/rGO$ composite electrode.

rGO composite electrode (after heat treatment). Both samples are smooth and uniform on the surface (Figure 2a,c). After being distorted by a tweezer, no powder flakes off the current collector, and no noticeable cracks are observed (Figure 2b,d). These results reveal that even without binders the adhesion and mechanical firmness of the electrodes are strong enough to be used for LIB anodes.

Figure 3 shows XRD patterns of Fe₂O₃ NP (starting material), Fe₂O₃/CNTs/GO composite electrode, and Fe₃O₄/CNTs/rGO composite electrode. Through EPD, Fe₂O₃ NPs, CNTs, and GO can be assembled on the Cu foil to obtain the Fe₂O₃/CNTs/GO composite electrode. The XRD pattern of Fe₂O₃/CNTs/GO composite electrode is exactly the same as that of pristine Fe₂O₃ NPs after subtracting the contribution from copper foil (marked as rhombic symbols), and both of them match well with the standard XRD data of Fe₂O₃ (Powder Diffraction File (PDF) No. 13-0534, Joint Committee on Powder Diffraction Standards (JCPDS), 1971). The small peak located at around 27° can be attributed to CNTs. The electronic conductivity of GO is relatively low. However, after heat treatment, it is effective to convert GO to rGO which is electrically conductive.³³ In this study, the Fe₂O₃/CNTs/GO composite electrode was annealed at 700 °C for 4 h under Ar atmosphere. Meanwhile, Fe₂O₃ in this composite film is reduced to Fe₃O₄ without damaging the structure of carbon materials (Figure S2), which can be wellindexed to cubic Fe₃O₄ (PDF No. 75-0449, JCPDS, 1971).



Figure 3. XRD patterns of $\rm Fe_2O_3$ nanoparticle, $\rm Fe_2O_3/CNTs/GO$ composite electrode and $\rm Fe_3O_4/CNTs/rGO$ composite electrode.

Raman spectroscopy was also carried out to confirm the presence of carbon in the Fe₃O₄/CNTs/rGO composite electrode (Figure 4a). The two prominent peaks at around 1353 and 1588 cm⁻¹ are attributed to D and G bands of the carbon (CNTs and rGO), which belong to the in-plane vibrations of strong disorder carbon and the in-plane vibrations of graphitic carbon, respectively.^{34–36} The small peaks located at around 484 and 668 cm⁻¹ can be ascribed to the T_{2g} and A_{1g} modes of Fe₃O₄, respectively.³⁷ A peak located at around 730 cm⁻¹ is also observed which is assigned to the A_{1g} mode of γ - $Fe_2O_3.^{38,39}$ The presence of $\gamma\text{-}\bar{Fe_2}O_3$ is explained by the oxidation of nanosized Fe₃O₄ particles induced by the thermal effect of laser irradiation.³⁷ In order to confirm the carbon content in the composite, the Fe₃O₄/CNTs/rGO composite film was detached from the Cu foil by ultrasonic treatment in water and freeze-dried and subsequently used for TG analysis (Figure 4b). The sample is heated to 900 °C in air so that Fe_3O_4 is oxidized to Fe_2O_3 and carbon (CNTs and rGO) is oxidized to CO2. The weight loss between 200 and 900 °C should be attributed to these two processes together. According to the remaining weight of Fe_2O_3 (72.9%), the original weight ratio of Fe_3O_4 in the composite is calculated to be 70.5% because the weight increment induced by Fe_3O_4 oxidized to Fe_2O_3 is 3.4%. This calculation method is also adopted in other previous reports about Fe₃O₄/C composites.^{6,17,2}f;

X-ray photoelectron spectra (XPS) measurements were also performed to further study the surface chemical nature of the composite electrodes (Figure 5). For the Fe₃O₄/CNTs/rGO composite electrode, there are four prominent peaks which are assigned to C, O, Fe, and Cu, respectively (Figure 5a). Figure 5b shows the Fe 2p high-resolution XPS spectrum of the Fe₃O₄/CNTs/rGO composite electrode. Two broad peaks at 725.2 and 711.2 eV corresponded to Fe $2p_{1/2}$ and Fe $2p_{3/2}$, respectively.^{20,40} The Fe $2p_{3/2}$ spectrum can be divided into two areas which correspond to Fe²⁺ (710.9 eV) and Fe³⁺ (712.9 eV), respectively.⁴¹ The fitting curve matches well with the original data. The satellite peak located between 715 and 722 eV is an important characteristic to distinguish between Fe₃O₄ and γ -Fe₂O₃.⁴² No evident satellite peak in this range is observed, indicating the presence of Fe_3O_4 in the $Fe_3O_4/$ CNTs/rGO composite electrode. 43,44 The C 1s high-resolution XPS spectrum of both electrodes can be deconvoluted into three peaks of 284.8 eV (nonoxygenated C, C-C), 286.0 eV (C-O), and 288.1 eV (C=O).⁴⁵ After annealing, the relative ratio of peak area of C-C bond to oxygen-containing bond



Figure 4. (a) Raman spectrum and (b) TG curve of the Fe₃O₄/CNTs/rGO composite electrode.



Figure 5. XPS spectra: (a) wide scan, (b) Fe 2p, and (c) C 1s for the as-prepared $Fe_3O_4/CNTs/rGO$ composite electrode. (d) XPS spectra of C 1s for the $Fe_2O_3/CNTs/GO$ composite electrode (without heat treatment).

(C–O and C==O) of the $Fe_3O_4/CNTs/rGO$ composite electrode (1.71) increases compared to that of the $Fe_2O_3/CNTs/GO$ composite electrode (0.94), which corroborates the reduction of GO to rGO.^{46,47}

The morphologies of the samples were then examined by SEM. Fe₂O₃ NPs (starting material) prepared by the hydrothermal thermal are well-dispersed with sizes of 100–200 nm (Figure S3). Many rGO sheets can be observed on the surface of the Fe₃O₄/CNTs/rGO composite electrode (Figure 6a). The rGO layers cover the surface of Fe₃O₄ NPs (Figure 6b), and Fe₃O₄ NPs are interconnected by CNTs (Figure 6c) to form an electronically conductive integrity. EDS mapping images (Figure 7) reveal that Fe₃O₄ NPs, CNTs, and rGO are homogeneously distributed. As shown in the cross-sectional SEM image (Figure 6d), it can be clearly seen that Fe₃O₄ NPs wrapped with CNTs are sandwiched by rGO layers in the composite. This specific structure not only enhances the electronic conductivity but also provides some buffer spaces to

accommodate the volume changes during lithiation/delithiation processes.

To better study the Fe₃O₄/CNTs/rGO composite structure, the composite film was detached from the Cu foil in ethanol through ultrasonication and used for TEM characterization. As shown in Figure 8a, Fe₃O₄ NPs and CNTs are anchored tightly to the rGO even after the ultrasonic treatment. CNTs construct an extended electronically conductive network interconnecting single Fe₃O₄ NPs (Figure 8b,c). The inset selected area electron diffraction (SAED) pattern exhibits rectangle symmetry dots and diffraction rings which can be attributed to the Fe₃O₄ nanocrystals and CNTs, respectively. It can be clearly observed that CNTs are attached on the surface of Fe_3O_4 in the HRTEM image (Figure 8d). The inside Fe_3O_4 NPs show obvious lattices with the interplanar distance of 0.25 nm, corresponding to (311) plane of cubic phase of Fe₃O₄. CNTs with curved lattices can be also observed on the surface of the particle. EDX mapping was also performed on the $Fe_3O_4/CNTs/rGO$ composite (Figure 8e). Fe and O are



Figure 6. SEM images of the $Fe_3O_4/CNTs/rGO$ composite electrode (a-c) on the surface and (d) on the cross section.



Figure 7. (a) SEM image and (b-f) corresponding elemental mapping of the Fe₃O₄/CNTs/rGO composite electrode.

uniformly distributed in the C, suggesting that Fe_3O_4 NPs are homogeneously decorated in the carbon matrix formed by CNTs and rGO.

The charge and discharge curves of the Fe₃O₄/CNTs/rGO composite and commercial Fe₃O₄ NPs electrodes in the voltage range of 0.01–3 V at 0.2 A g⁻¹ are shown in Figure 9a,b, respectively. Both samples show an obvious voltage plateau at around 0.8 V in the first discharge process corresponding to the reaction Fe₃O₄ + 8Li⁺ + 8e⁻ \rightarrow 3Fe⁰ + 4Li₂O.⁴⁸ However, the second discharge profile is different, indicating that the irreversible reactions occurred during the first cycle.⁴⁹ The Fe₃O₄/CNTs/rGO composite electrode exhibits initial discharge/charge of 1358 and 966 mAh g⁻¹, corresponding to the

initial Coulombic efficiency (CE) of 71.1%. Although commercial Fe₃O₄ NPs electrode delivers a higher initial discharge/charge of 1681 and 1205 mAh g⁻¹, the charge and discharge curves decay quickly during cycling. No obvious change in the charge and discharge profiles of the Fe₃O₄/CNTs/rGO composite electrode is observed during cycling, indicating the superior cycling stability.^{6,50}

The cycling performances of both samples at 0.2 A g^{-1} are shown in Figure 9c. The discharge capacity of the Fe₃O₄/ CNTs/rGO composite electrode is 1048 mAh g^{-1} after 50 cycles, which is much higher than that of commercial Fe₃O₄ NPs electrode (174 mAh g^{-1}). The CE of the Fe₃O₄/CNTs/ rGO composite electrode remained above 98% since the



Figure 8. (a–c) TEM images of the $Fe_3O_4/CNTs/rGO$ composite; the inset is the corresponding SAED pattern. (d) HRTEM image and (e) dot mapping (C, Fe, and O) of the $Fe_3O_4/CNTs/rGO$ composite.

second cycle, but that of commercial Fe₃O₄ NPs electrode slowly increases to 98% until the 35th cycle, indicating the much improved electronic conductivity of the Fe₃O₄/CNTs/ rGO composite electrode. It should be noted that the specific capacity of Fe₃O₄/CNTs/rGO composite electrode exceeds the theoretical capacity of Fe₃O₄ (928 mAh g⁻¹). The enhanced reversible capacity probably results from the following: (1) The formation of polymer-like film (as shown in Figure S4) owing to the activated electrolyte degradation can deliver an excess "pseudocapacitance-type" capacity.^{20,51–53} (2) The pulverized particles of Fe₃O₄ NPs maintaining good electrical contact with the carbon matrix can increase contact areas between the electrode and electrolyte and provide more active sites for Li⁺ ions insertion.^{5,54} The rate tests of the $Fe_3O_4/CNTs/rGO$ composite electrode were carried out at various current densities ranging from 0.2 to 10 A g⁻¹. The $Fe_3O_4/CNTs/rGO$ composite electrode has discharge capacity values of 970, 900, 828, 748, and 643 mAh g⁻¹ at 0.2, 0.5, 1, 2, and 5 A g⁻¹, respectively. Even at a very high current density of 10 A g⁻¹ (about 7 min to finish every charge/discharge cycle), a high reversible capacity of 540 mAh g⁻¹ can be still obtained. When the current density returns to 0.2 A g⁻¹, the discharge capacity can recover to 1010 mAh g⁻¹, indicating the good reversibility.

Long-term cyclic performance is another important property to LIB anodes. The $Fe_3O_4/CNTs/rGO$ composite electrode was cycled at 0.2 A g⁻¹ for the first 5 cycles and then cycled at the high current density (1 A g⁻¹) for subsequent 450 cycles.



Figure 9. Discharge and charge curves of (a) $Fe_3O_4/CNTs/rGO$ composite electrode and (b) commercial Fe_3O_4 NPs electrode at 0.2 A g^{-1} . (c) Capacity retention and Coulombic efficiency of the $Fe_3O_4/CNTs/rGO$ composite electrode at 0.2 A g^{-1} . (d) Rate performance of the $Fe_3O_4/CNTs/rGO$ composite electrode at 0.2 A g^{-1} . (d) Rate performance of the $Fe_3O_4/CNTs/rGO$ composite electrode at $1.2 \text{ A } g^{-1}$. (d) Rate performance of the $Fe_3O_4/CNTs/rGO$ composite electrode at $1.2 \text{ A } g^{-1}$. (e) Long-term cycling performance of the $Fe_3O_4/CNTs/rGO$ composite electrode at 1 A g^{-1} . The specific capacity of the $Fe_3O_4/CNTs/rGO$ composite electrode is calculated by the total weight of the composite film deposited on the Cu foil.

The discharge capacity of 1080 mAh g⁻¹ is obtained after 450 cycles at 1 A g⁻¹. The Fe₃O₄/CNTs/rGO composite electrode shows a rapid capacity increase from the 125th to 235th cycles. Such a phenomenon of the gradual increase of capacity with cycling has also been observed in many Fe₃O₄ and other metal oxide anode materials.^{20,55–59} Nanosized metal oxide particles may promote the formation of a polymer-like film on the particles surface, which can provide extra capacitive-like capacity in long-term cycling.^{52,53,56,59–61} Besides, cycle performance of the contrastive electrodes without Fe₃O₄ or carbon materials (GO and CNTs) were also investigated (Figure S5).

The EIS of the electrodes after the first cycle is shown in Figure 10. Each plot is composed of two compressed semicircles between the high- and middle-frequency regions and a straight line in the low-frequency region. Both spectra were fitted by using the equivalent circuit model (inset of Figure 10), with R_s representing the electrolyte resistance, R_1 and CPE₁ representing the resistance and capacitance of the SEI film, R_2 and CPE₂ representing the charge-transfer resistance and double-capacitance on the particles surface,



Figure 10. EIS and fitting results of the $Fe_3O_4/CNTs/rGO$ composite and commercial Fe_3O_4 NPs electrodes; inset is the equivalent circuit used for fitting.

and $W_{\rm o}$ representing the diffusion of Li⁺ ions.^{11,62} The fitting results are listed in Table 2. The difference is clearly seen in that R_1 and R_2 values of the Fe₃O₄/CNTs/rGO composite electrode are much smaller than that of commercial Fe₃O₄ NPs electrode, indicating the faster transportation of Li⁺ ions and

 Table 2. Equivalent-Circuit Parameters Obtained from

 Fitting the Experimental Impedance Spectra

sample	$R_{\rm s} (\Omega)$	$R_1(\Omega)$	$R_2(\Omega)$
commercial Fe ₃ O ₄ NPs	1.771	23.74	171.6
Fe ₃ O ₄ /CNTs/rGO	1.674	14.93	22.68

electrons in this specific structure, thus resulting in superior rate performance.

The enhanced electrochemical performance of the $Fe_3O_4/$ CNTs/rGO composite electrode can be summarized to two main reasons. First, Fe₃O₄ NPs are interconnected by CNTs and sandwiched by rGO layers to form a robust network with high electronic conductivity. Second, voids between Fe₃O₄ NPs and the flexible CNTs and rGO layers can buffer well the volume changes during cycling to ensure good structural stability. This can be further proved by the SEM and TEM images of Fe₃O₄/CNTs/rGO composite after cycling (Figure S6). After 50 cycles, the surface of the electrode is covered with gel-like film combined with the SEI layer. Many small voids which act as buffer spaces during cycling can be still observed, and the Fe₃O₄ NPs interconnected by CNTs are still tightly anchored to the rGO. The well-retained buffer spaces and conductive channel can further explain enhanced electrochemical performance of as-prepared Fe₃O₄/CNTs/rGO composite electrode.

4. CONCLUSIONS

The binder-free $Fe_3O_4/CNTs/rGO$ composite electrode has been successfully fabricated through the facile EPD route and subsequent heat treatment. The unique structure with Fe_3O_4 NPs interconnected by CNTs and anchored on the rGO layers effectively accommodates the volume changes during lithiation/ delithiation processes and enhances the electronic conductivity of the electrode. Consequently, the $Fe_3O_4/CNTs/rGO$ composite exhibits an excellent cycling stability (reversible capacity of 1080 mAh g⁻¹ after 450 cycles at 1 A g⁻¹). Moreover, even at a very high current density of 10 A g⁻¹, the high capacity of 540 mAh g⁻¹ can be still obtained, indicating the good potentials for the application of this composite electrode for high-performance LIB anode.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b07990.

SEM images of commercial Fe₃O₄ NPs. SEM and TEM images of the contact areas between Fe₃O₄ NPs, CNTs, and rGO in the Fe₃O₄/CNTs/rGO composite. SEM images of Fe₂O₃ NPs. TEM image of a single Fe₃O₄ NP after 50 cycles in Fe₃O₄/CNTs/rGO electrode. Cycle performance of the contrastive electrodes without Fe₃O₄ or carbon materials. SEM and TEM images of Fe₃O₄/CNTs/rGO composite after 50 cycles. (PDF)

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Notes

The authors declare no competing financial interest.

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