

High Rate Performance of Aqueous Magnesium-iron-ion Batteries Based on Fe₂O₃@GH as the Anode^①

SHAO Shuang-Xi^② CANG Rui-Bai^② YE Ke^③ GAO Yin-Yi
ZHU Kai YAN Jun WANG Gui-Ling CAO Dian-Xue^③

(Key Laboratory of Superlight Materials and Surface Technology of Ministry of Education, College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China)

ABSTRACT Aqueous Mg-ion batteries (MIBs) are safe, non-toxic and low-cost. Magnesium has a high theoretical specific capacity with its ion radius close to that of lithium. Therefore, aqueous magnesium ion batteries have great research advantages in green energy. To acquire the best electrode materials for aqueous magnesium ion batteries, it is necessary for the structural design in material. Fe₂O₃ is an anode material commonly used in Li-ion battery. However, the nano-cube Fe₂O₃ combined with graphene hydrogels (GH) can be successfully prepared and employed as an anode, which is seldom researched in the aqueous batteries system. The Fe₂O₃/GH is used as anode in the dual MgSO₄ + FeSO₄ aqueous electrolyte, avoiding the irreversible deintercalation of magnesium ions. In addition, the Fe element in anode material can form the Fe³⁺/Fe²⁺ and Fe²⁺/Fe³⁺ redox pairs in the MgSO₄ + FeSO₄ electrolyte. Thus, the reversible insertion/(de)insertion of magnesium and iron ions into/from the host anode material can be simultaneously achieved. After the initial charge, the anodic structure is changed to be more stable, avoiding the formation of MgO. The Fe₂O₃/GH demonstrates high rate properties and reversible capacities of 198, 151, 121, 80, 75 and 27 mAh g⁻¹ at 50, 100, 200, 300, 500 and 1000 mA g⁻¹ correspondingly.

Keywords: aqueous battery, Mg ion, Fe₂O₃/graphene hydrogels, anode material, FeSO₄;

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1 INTRODUCTION

Recently, magnesium ion battery has aroused more and more attention, in which not only the ion radius of magnesium is similar to that of lithium but also magnesium is low cost and abundant resources on the earth. Aqueous Mg-ion batteries (MIBs) attract much attention due to their high theoretical capacity and abundant resource^[1]. The aqueous MIBs play an important role in the development of green energy compared with no-aqueous MIBs^[2], because of their advantages of low cost, safety, stability, and sustainable development. The aqueous MIBs electrolyte comes from aqueous and inorganic magnesium salt. Since the first aqueous rechargeable battery was produced by SONY in 1994^[3], most cathode materials such as MnO₂, LiMn₂O₄ and

Na_{0.44}MnO₂ have been used in lithium/sodium battery^[4-8]. For the development of cathode materials, various cathode materials such as transition metal chalcogenides/oxides, polyanion compounds, and Prussian blue are synthesized as a capable host for Mg ion storage^[9]. Among them, manganese oxide has become an interesting research subject and a capable host for MIBs owing to its high capacity (~200 mAh g⁻¹), suitable working voltage and low cost^[10-12]. In contrast, the progress in anode materials is slow and lack of capable anode materials, which seriously hinders the potential applications of aqueous MIBs^[13-16]. Zhang et al. reported FeVO₄ nanomaterials as anodes for aqueous MIBs with a capacity of 140 mAh g⁻¹^[17]. Unfortunately, their low capacity is difficult to match with manganese oxide cathode well and the structural collapse of pure materials results in a continuous

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② These authors contributed equally to this work

③ Corresponding authors. E-mails: yeke@hrbeu.edu.cn (Ye K.) and caodianxue@hrbeu.edu.cn (Cao, D. X)

capacity decay during the Mg (de)intercalation process. Thus, there is a challenge to identify an inexpensive anode with a large capacity and highly reversible charge storage mechanism in an aqueous electrolyte^[18–20]. The controlled morphology of materials can effectively improve the electrochemical properties of materials. Nano Fe₂O₃ materials with special cubic structures because of its high theoretical capacity are used as an anode material having excellent properties (924 mAh g⁻¹), low cost, low toxicity and natural abundance of iron^[21–23]. Unfortunately, lithiation large volume expansion, poor electronic conductivity and ion diffusion capacity are major problems limiting the practical applicability of these negative electrode materials^[24, 25].

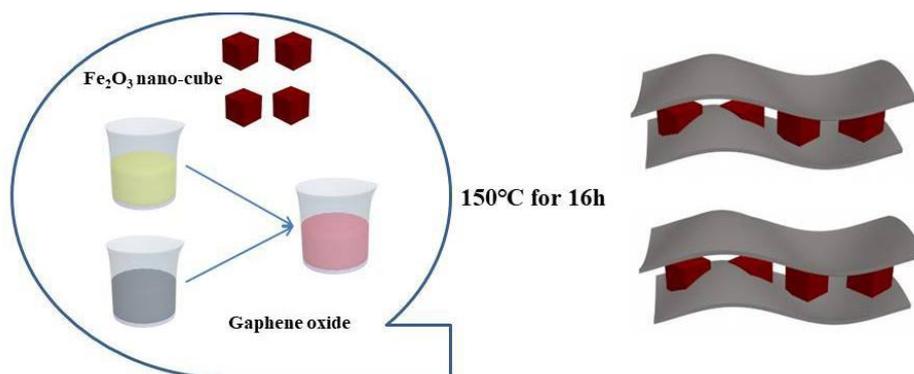
According to the reports, the design and manufacture of particles have a special form and customized performance that can be enhanced by cycling performance and rate capability. The Fe₂O₃-based anode materials were used in the non-aqueous battery, because iron metal batteries are extremely competitive in their cost and iron possesses an attractive electrochemical property. Via the two-electron transfer, iron theoretically delivers a high specific capacity of ~960 mAh g⁻¹ and an outstanding volumetric capacity of ~7557 mAh cm⁻³, both of which are higher than those for other electrode materials like P₂-Mg_{1/3}Ni_{1/3}Mn_{2/3}O₂ electrode at 1.0 C in 1.0 M MgSO₄ (101.4 mAh g⁻¹), Mg(NO₃)₂ (99.7 mAh g⁻¹), and MgCl₂ (117.0 mAh g⁻¹) electrolytes and NaTi(PO₄)₃ as an anode at 0.78 C in 1.0 M NaNO₃ electrolyte (121 mAh g⁻¹)^[26, 27]. However, when the Fe₂O₃-based materials were used as anode or Fe₂O₃ as a cathode in aqueous MIBs, the magnesium ion can't insert/(de)insert in Fe₂O₃ but can only stick to Fe₂O₃. The above-mentioned iron-base anode materials show considerable interests on the Fe-metal flow batteries, where the cathode and anode operate on the Fe³⁺/Fe²⁺ and Fe²⁺/Fe³⁺ redox couples, respectively. Herein, we prepared the Fe₂O₃ and Fe₂O₃/graphene hydrogels (GH) anodes. The Fe₂O₃/GH displayed a capacity of 198 mAh g⁻¹ in the aqueous MgSO₄ + FeSO₄ electrolyte for Mg-Fe ion battery, indicating an excellent storage capacity of magnesium and iron ions. All the above clearly reveal that Fe₂O₃/GH is an excellent anode material for high-performance Mg-Fe-ion battery and an important step in the development of an aqueous Mg-Fe-ion battery. This battery shows higher rate properties than other aqueous batteries^[28–30], delivering the reversible capacity of

198 mAh g⁻¹ at a current density of 50 mA g⁻¹. This result also lays theoretical foundation for the application of aqueous magnesium-iron ion batteries.

2 EXPERIMENTAL

2.1 Preparation and characterization of Fe₂O₃ and Fe₂O₃/GH

The typical synthesis of FeCl₃ 6H₂O was dissolved in ethanol and DI water under vigorously magnetic stirring, during which sodium acetate was added until complete dissolution. Then, the mixture was sealed in a Teflon-lined stainless-steel autoclave and maintained at 180 °C for 12 h. After cooling to room temperature, the products were formed as red solution and washed several times by DI water and ethanol, and the final dark red products were dried at 60 °C for overnight. Subsequently, the obtained Fe₂O₃/GH was utilized for fabricating Fe₂O₃/GH composite. The process of recombination of Fe₂O₃ and graphene composite is as follows. Firstly, for the preparation of solution A, graphene oxide was dissolved in DI-water and added into ethylenediamine with good stirring and even distribution. Secondly, Fe₂O₃ nanocubes were dissolved in DI-water to form solution B. Thirdly, solutions A and B were mixed and fully ultrasonicated to make the Fe₂O₃ nano-cubes uniformly disperse in the mixed solution (Scheme 1). Such a self-assembled composite is advantageous in the cubic structure of Fe₂O₃ nanoparticles and graphene can keep its original topography. Furthermore, it is noted that, after a hydrothermal reaction by freeze-drying procedures. The microstructure of composite can be easily controlled by graphene oxide, because the graphene sheet with a high surface area can effectively prevent the aggregation of Fe₂O₃ nanocube. Furthermore, the addition of Fe₂O₃ can effectively prevent the accumulation of graphene sheets, which can obtain the composite material with a high surface area. Meantime, the Fe₂O₃/GH nano-cubes composite with loose porous structure by freeze-drying process can enhance pore volume. Fe₂O₃/GH composite material having a high surface area and high electrical conductivity is a promising electrode material, so it can provide a large surface area of electrochemical reaction and discharging/charging process to provide several active Mg and Fe ion diffusions.



Scheme 1. An illustration for the formation of $\text{Fe}_2\text{O}_3/\text{GH}$

2.2 Electrochemical measurement of

Fe_2O_3 and $\text{Fe}_2\text{O}_3/\text{GH}$

The slurry of the anode was constituted by mixing 10% polyvinylidene difluoride (PVDF) binder, 10% acetylene black and 80% Fe_2O_3 and $\text{Fe}_2\text{O}_3/\text{GH}$. The carbon fiber cloth with a size of $1.2\text{ cm} \times 1.2\text{ cm}$ is used to coat the above slurry under vacuum drying at $80\text{ }^\circ\text{C}$ for 24 h.

3 RESULTS AND DISCUSSION

X-ray diffraction (XRD) gives the institute composite phase structure and phase purity (Fig. 1). The major diffraction peaks of Fe_2O_3 (brown line) and $\text{Fe}_2\text{O}_3/\text{GH}$ (ginger line) can be well indexed to the phase of Fe_2O_3 (hematite, JCPDS33-0664). Comparing these two curves, the contrast between $\text{Fe}_2\text{O}_3/\text{GH}$ and Fe_2O_3 shows a new peak at about 26.6 , which is from graphene^[31]. This result proves that $\text{Fe}_2\text{O}_3/\text{graphene hydrogel (GH)}$ successfully recombines.

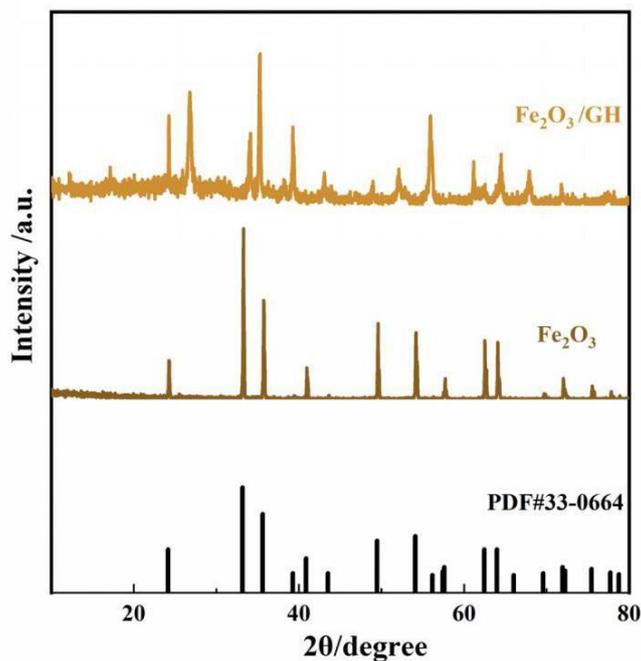


Fig. 1. XRD patterns of Fe_2O_3 and $\text{Fe}_2\text{O}_3/\text{GH}$

It has come to light that graphene is an electrode material with high conductivity and large specific surface area. Therefore, we prepared the Fe_2O_3 and graphene composite using as an anode to improve the electrochemical properties. Fig. 2 shows the SEM images of Fe_2O_3 and $\text{Fe}_2\text{O}_3/\text{GH}$. In

Figs. 2a and 2b, Fe_2O_3 is the regular cube material. In Figs. 2c and 2d, the Fe_2O_3 anode materials demonstrate an average size less than 100 nm. Figs. 2e and 2f show the $\text{Fe}_2\text{O}_3/\text{GH}$ image. A graphene sheet structure is clearly visible and the Fe_2O_3 is non-uniformly distributed on the sheet.

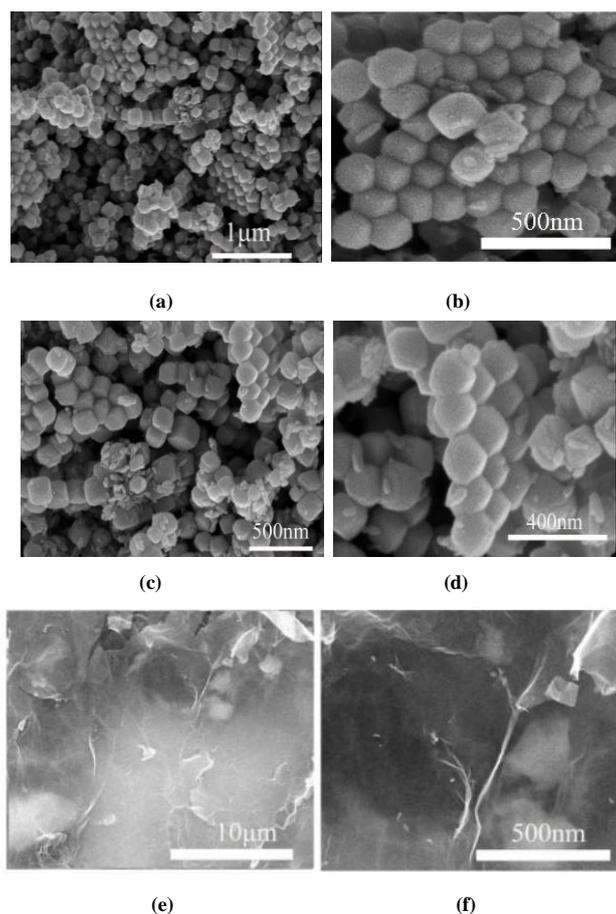


Fig. 2. SEM images of Fe_2O_3 (a~d) and $\text{Fe}_2\text{O}_3/\text{GH}$ (e~f)

Fe_2O_3 and $\text{Fe}_2\text{O}_3/\text{GH}$ are used as an anode material in 0.5 M MgSO_4 and 0.5 M $\text{MgSO}_4 + \text{FeSO}_4$ aqueous electrolyte for the working electrode. The cyclic voltammetry (CV) curves of Fe_2O_3 and $\text{Fe}_2\text{O}_3/\text{GH}$ electrodes with a voltage window of $-1.1 \sim 0.5$ V at a scan rate of 3.0 mV s^{-1} are shown in Fig. 3. Fig. 3a displays the Fe_2O_3 as an anode in 0.5 M MgSO_4 aqueous solution, showing a cathodic peak at 0.0 V and three anodic peaks at -0.38 , -0.30 and 0.08 V, respectively. In the CV curves, Mg ion is inserted in the electrode material, but Mg ion can't insert/(de)insert in the Fe_2O_3 nano-cube material during charge and discharge process. Fig. 3b shows the Fe_2O_3 anode materials in 0.5 M $\text{MgSO}_4 + \text{FeSO}_4$ aqueous solution, which has only two cathodic peaks at 0.26/ -0.18 V and an anodic peak at -0.86 V. The whole peak-current potential shifts to the left direction with an obvious plating phenomenon. To further solve the above problems, the $\text{Fe}_2\text{O}_3/\text{GH}$ was used as an anode in 0.5 M MgSO_4 (Fig. 3c), which had two cathodic peaks at 0.15/ -0.30 V and an anodic peak at -0.78 V with the polarization phenomenon disappearing significantly. The anode is still a quasi-reversible process, because Mg ion is

only inserted at the Fe_2O_3 material in discharge. During charging, the Mg ions can't be released from the Fe_2O_3 material to form an irreversible state. Fig. 3d shows the $\text{Fe}_2\text{O}_3/\text{GH}$ as an anode in $\text{MgSO}_4 + \text{FeSO}_4$ with a reversible system, which has two anodic peaks at $-0.6/-0.3$ V and cathodic peaks at $-0.16/-0.46$ V with potentials in safe voltage ranges. The insertion/(de)insertion process of Mg and Fe ions into/from $\text{Fe}_2\text{O}_3/\text{GH}$ material results from the donor and acceptor of electrons accompanied with Mg^{2+} ion insertion/(de)insertion process into/from the lattice of $\text{Fe}_2\text{O}_3/\text{GH}$, in which the catholyte and anolyte operate on $\text{Fe}^{2+}/\text{Fe}^{3+}$ with the multi-step Mg/Fe-ion storage process. Electrochemical kinetics of the reaction at particular electrode can be determined from the voltage difference between the redox peaks. The Fe_2O_3 was used as an anode in MgSO_4 and $\text{MgSO}_4 + \text{FeSO}_4$ aqueous solution, and the voltage gaps between the redox peaks are 0.51 and 0.81 V, respectively. For $\text{Fe}_2\text{O}_3/\text{GH}$ as an anode in MgSO_4 and $\text{MgSO}_4 + \text{FeSO}_4$ aqueous solution, the voltage gaps between the redox peaks are 0.72 and 0.51 V, respectively. Thus, the $\text{Fe}_2\text{O}_3/\text{GH}$ in $\text{MgSO}_4 + \text{FeSO}_4$ decreased the electrode

polarization, which is advantageous for the electrochemical reaction. Meanwhile, the Fe₂O₃/GH anode materials in

MgSO₄ + FeSO₄ reveal preferable electrochemical properties than other electrodes according to the peak currents.

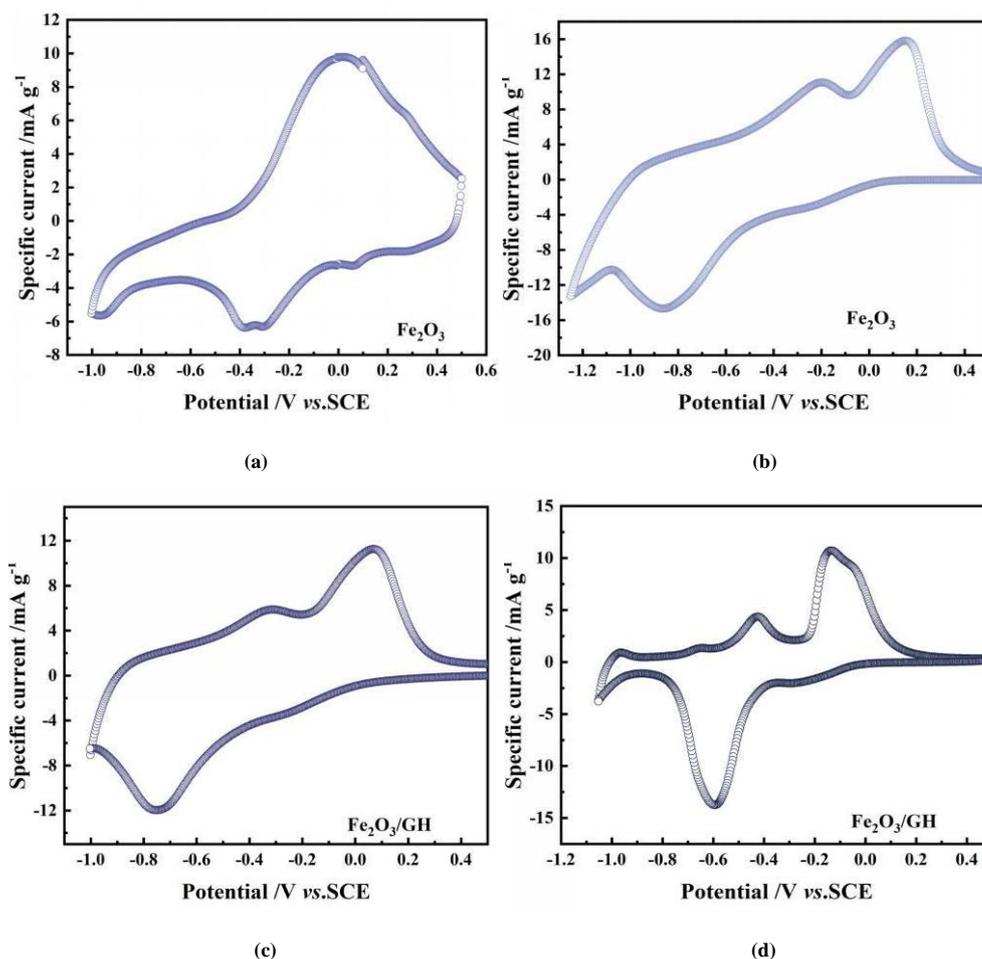


Fig. 3. CVs of Fe₂O₃ electrode in 0.5 M MgSO₄ (a) and 0.5 M MgSO₄ + FeSO₄ (b) electrolyte, respectively; Fe₂O₃/GH electrode in 0.5 M MgSO₄ (c) and 0.5 M MgSO₄ + FeSO₄ (d) electrolyte, respectively

To further study the electrochemical properties of Fe₂O₃ and Fe₂O₃/GH, the galvanostatic charge-discharge measurements were tested in the voltage window of -1.0 to 0.4 V. Fig. 4a shows the Fe₂O₃ as an anode at 100 mA g⁻¹ with the initial cycle discharge specific capacity of 38 mAh g⁻¹ in 0.5 M MgSO₄ and the coulombic efficiency close to 100%. In addition, Fe₂O₃ was used as anode within the voltage window of -0.85 to 0.1 V in MgSO₄ + FeSO₄ at 100 mA g⁻¹ and its discharge specific capacity was 131 mAh g⁻¹ (Fig. 4b). Although there is a certain improvement in specific capacity, the coulombic efficiency is weak with 91%. The discharge/charge curves of Fe₂O₃/GH as an anode in MgSO₄ with the capacity of 400 mAh g⁻¹ and coulombic efficiency of 62.5% are shown in Fig. 4c. After improving the

conductivity of the electrode, the capacity is increased and verified before CV test. Mg ion is only inserted in the Fe₂O₃ material in discharge. During the charging process, Mg ion can't be released from the iron material to form an irreversible state. When the Fe₂O₃/GH was used as an anode in MgSO₄ + FeSO₄, it had an outstanding performance with the discharge specific capacity of 155 mAh g⁻¹ and coulombic efficiency close to 100% at a current density of 100 mA g⁻¹. Meanwhile, the potential of the discharge plateau is almost identical to that of CV. The Fe₂O₃/GH as an anode in 0.5 M MgSO₄ + FeSO₄ aqueous solution can not only avoid the phenomenon of hydrogen and oxygen evolution but also improve the electrochemical performance and stability to a certain extent.

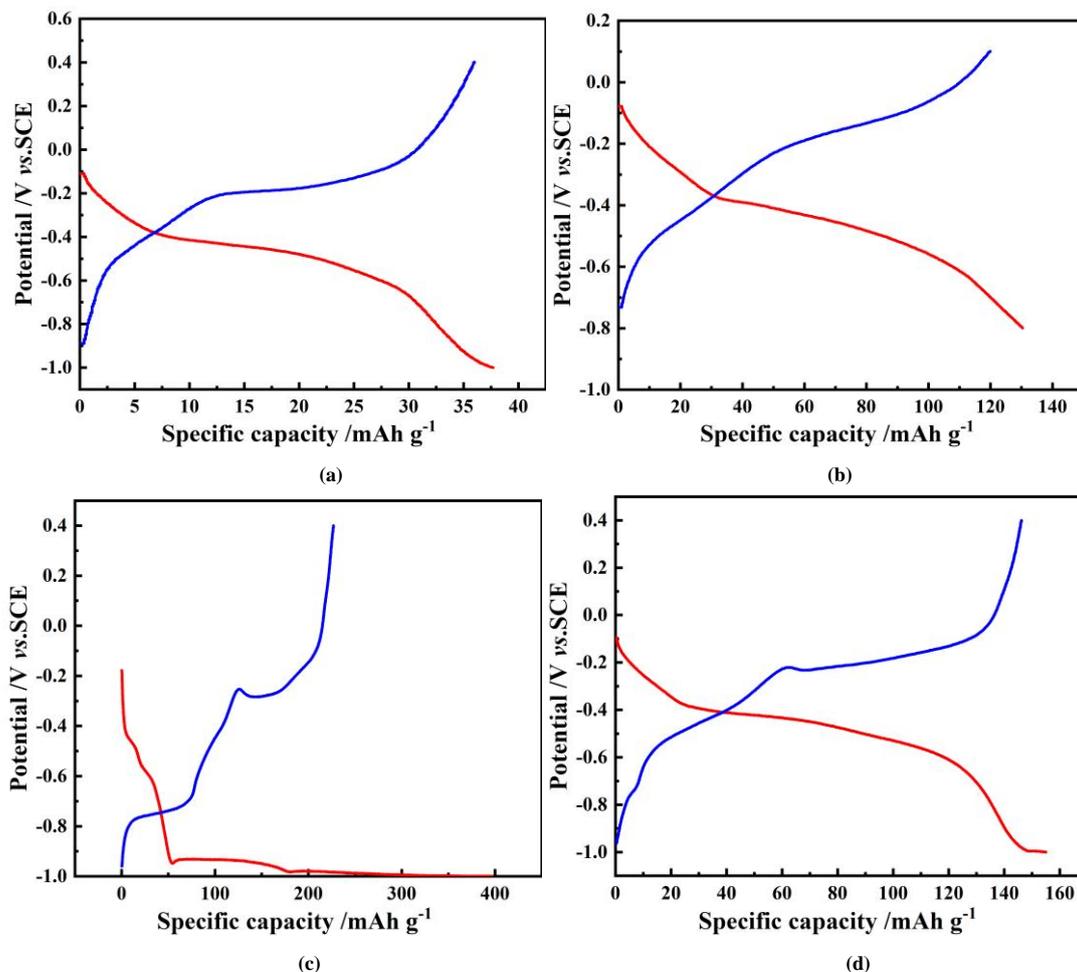


Fig. 4. Galvanostatic charge and discharge curves of Fe_2O_3 anode in 0.5 M MgSO_4 (a) and 0.5 M $\text{MgSO}_4 + \text{FeSO}_4$ (b) electrolyte, respectively; $\text{Fe}_2\text{O}_3/\text{GH}$ anode in 0.5 M MgSO_4 (c) and 0.5 M $\text{MgSO}_4 + \text{FeSO}_4$ (d) electrolyte, respectively

Electrochemical impedance spectroscopic (EIS) measurement of Fe_2O_3 and $\text{Fe}_2\text{O}_3/\text{GH}$ in $\text{MgSO}_4 + \text{FeSO}_4$ is shown in Fig. 5. The main purpose of the EIS test is to further verify the diffusion rate of the Fe_2O_3 and $\text{Fe}_2\text{O}_3/\text{GH}$ material in the electrolyte at room temperature. Fig. 5a shows the impedance spectra of Fe_2O_3 and $\text{Fe}_2\text{O}_3/\text{GH}$ electrodes. In the high-frequency region, the partial semicircle indicates a charge transfer resistance (R_{ct}) and the intercept indicates the internal resistance (R_s). In low-frequency region, the linear portion represents the Warburg impedance, which is utilized to determine the diffusion coefficient of magnesium-iron ions in the electrode. Therefore, the model circuit (inset of Fig. 5a) is fitted by ZView software and the relevant parameters are listed in Table 1. Fig. 5b shows the curve of Z_{Re} as a function of $\omega^{-1/2}$, depending on the slope of linear portion of the

low-frequency region. Therefore, the magnesium-iron ion diffusion coefficient ($D_{\text{Mg}^{2+}}$) can be obtained by Eqs. (1) and (2) as below:

$$D_{\text{Mg}^{2+}} = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma^2} \quad (1)$$

$$Z_{\text{Re}} = R_s + R_{\text{ct}} + \sigma \omega^{-1/2} \quad (2)$$

where $D_{\text{Mg}^{2+}}$ is the magnesium-iron ion diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), F is the Faraday constant, R is the gas constant, T is the room temperature (25 °C), A is the surface area of the electrode, n is the number of transferred electrons ($n = 1$), σ is the slope of Z_{Re} against $\omega^{-1/2}$ plot, and C is the concentration of the magnesium-iron ion.

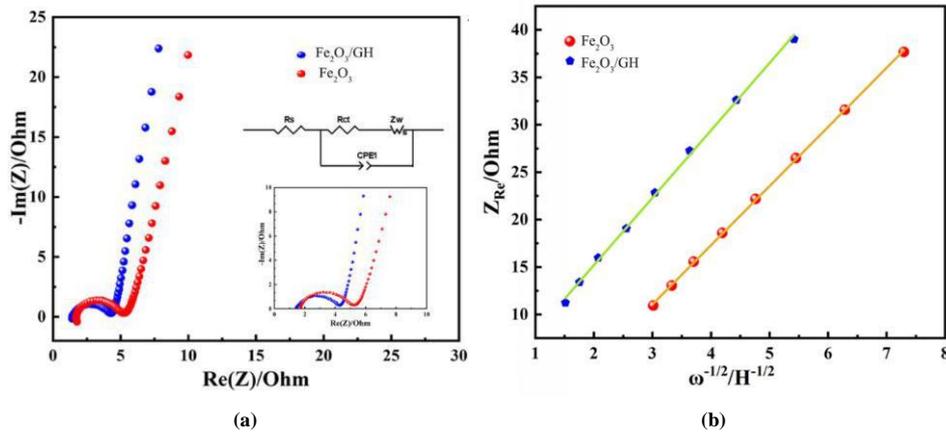


Fig. 5. Impedance spectra of the Fe₂O₃ and Fe₂O₃/GH electrodes (a); the slope of Z_{Re} against $\omega^{-1/2}$ plot (b)

In Table 1, the internal resistance R_s values of the two electrodes are a little different. The charge-transfer resistance R_{ct} value of Fe₂O₃/GH is much smaller than that of the Fe₂O₃ electrode, because the Fe₂O₃/GH composite owns a larger specific surface area and higher electrical conductivity derived from the GH property and more beneficial for the charging process. Z_{Re} is derived from Eq. (2) and the diffusion

coefficient $D_{Mg^{2+}}$ can be calculated from Eq. (1). The $D_{Mg^{2+}}$ value of Fe₂O₃/GH electrode is much larger than that of the Fe₂O₃ electrode, proving that magnesium-iron ions diffuse faster onto the surface of electrode. In consequence, R_s and R_{ct} of the Fe₂O₃/GH electrode shows a smaller value. The large $D_{Mg^{2+}}$ value indicates a good electrochemical kinetics.

Table 1. Evaluated Impedance Parameter Values of the Two Electrodes in 0.5 M MgSO₄ + FeSO₄ Electrolyte from EIS of Fig. 5

Sample	R_s (Ω)	DMg^{2+} ($cm^2 s^{-1}$) $\pm 0.01 E^{-15}$	CPE-T	CPE-P	Sample
Fe ₂ O ₃	3.52	$8.88 E^{-15}$	$9.23 E^{-5}$	0.98	Fe ₂ O ₃
Fe ₂ O ₃ /GH	3.16	$9.65 E^{-15}$	$9.77 E^{-5}$	0.90	Fe ₂ O ₃ /GH

The Fe₂O₃/GH anode displays a high rate capability and superior cycle ability. Fig. 6 shows the Fe₂O₃/GH electrode charge/discharges in the potential region from -1.0 to 0.4 V at different currents in MgSO₄ + FeSO₄ electrolyte. Fig. 6a depicts the rate performance of Fe₂O₃/GH as an anode. The Fe₂O₃/GH exhibits the capacities of 198, 155, 121, 80, 75 and 27 mAh g⁻¹ at 50, 100, 200, 300, 500 and 1000 mA g⁻¹, respectively. All the discharge curves in Mg-Fe ion electrolyte exhibit a large potential plateau at around -0.4 and -0.6 V, which are associated with the insertion of Mg²⁺ into the lattice of Fe₂O₃/GH and the process of Fe³⁺ to Fe²⁺. The charge potential plateau appears at around -0.2 and 0.1 V, which are associated with the (de)insertion of Mg²⁺ from the lattice of Fe₂O₃/GH and process of Fe²⁺ to Fe³⁺, demonstrating a capable rate performance of Fe₂O₃/GH as an anode in 0.5 M MgSO₄ + FeSO₄ aqueous solution. Meanwhile, at a current

density of 100 mA g⁻¹, Fe₂O₃/GH anode exhibits a discharge specific capacity of 165 mAh g⁻¹ at the initial cycle with a capacity retention of 89.3% after 200 cycles, suggesting an outstanding cycling stability (Fig. 6c). It is noted that, after 200 cycles, the respective capacity retention is close to 100%, demonstrating the most excellent cycle stability in MgSO₄ + FeSO₄ aqueous solution. The Mg-Fe ions are converted into the insertion without structural collapse with a reversible process. The electrochemical performance is prior to that of other aqueous-based batteries, such as 150 mAh g⁻¹ of Mg-bir/CC in 0.5 M Mg(ClO₄)₂^[31], 90 mAh g⁻¹ of 400-MgMn₂O₄ in 3.0 M Mg(NO₃)₂^[32], 51 mAh g⁻¹ of CuFe-PBA in 1.0 M Mg(NO₃)₂^[33] and 59.2 mAh g⁻¹ of polypyrrole (PPy)-coated MoO₃^[34], which provides a new member for aqueous battery family (as listed in Table 2 and Table S1)^[34-38].

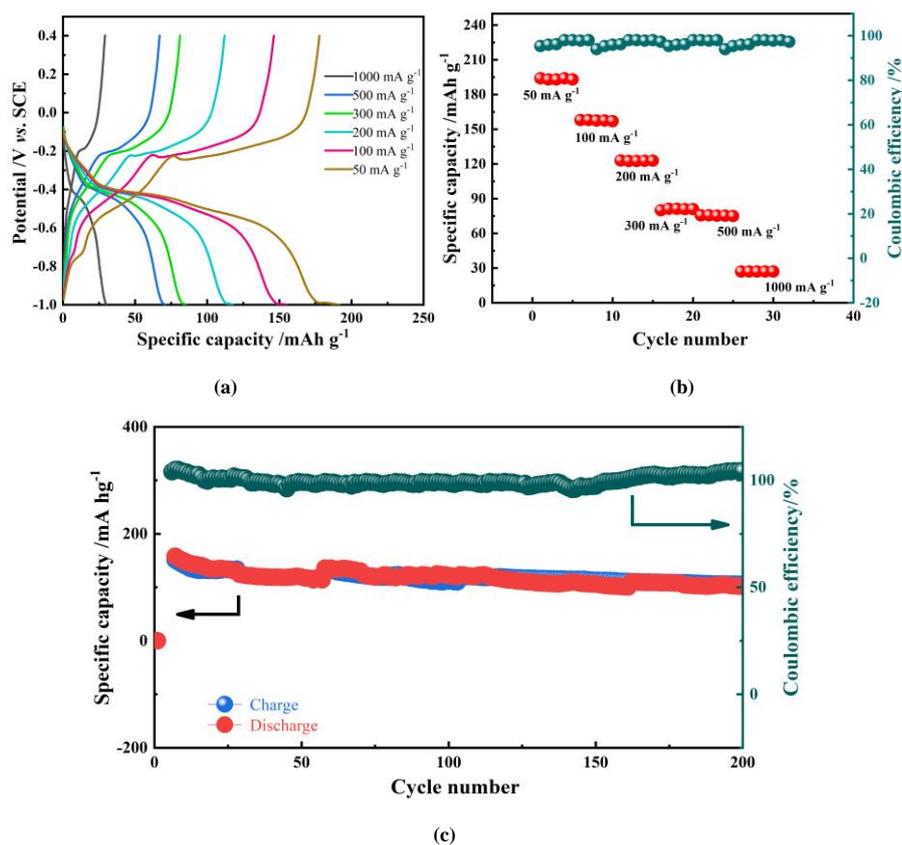


Fig. 6. Rate performance of $\text{Fe}_2\text{O}_3/\text{GH}$ electrode (a and b); the cycle performance of $\text{Fe}_2\text{O}_3/\text{GH}$ electrode (c) in $0.5 \text{ M MgSO}_4 + \text{FeSO}_4$ electrolyte

Table 2. Comparison of Our Rechargeable Battery with State-of-the-art Works in Terms of Electrode, Electrolyte and Capacity

Electrode	Electrolyte	Capacity (mAh g^{-1})	Ref.
TiO_2	Aqueous	75	12
Mg-bir/CC	$\text{Mg}(\text{ClO}_4)_2$	150	31
$\text{Na}_3\text{V}_2(\text{PO}_4)_3$	NaNO_3	112	36
(PPy)-coated/ MoO_3	Aqueous	59	34
$\text{TiO}_2/\text{graphene}$	Aqueous	30	35
400- MgMn_2O_4	$\text{Mg}(\text{NO}_3)_2$	90	32
CuFe-PBA	$\text{Mg}(\text{NO}_3)_2$	51	33
$\text{Na}_2\text{Ti}(\text{PO}_4)_3$	NaNO_3	121	27
$\text{V}_2\text{O}_5/\text{GA}$	MgSO_4	75	21
FeVO_4	MgSO_4	118	17
$\text{Fe}_2\text{O}_3/\text{GH}$	$\text{MgSO}_4 + \text{FeSO}_4$	198	This work

In order to further determine the composition of the composite material and electrochemical reaction changes, XPS measurement is performed to explore the change of magnesium-iron ions during the charging and discharging process of $\text{Fe}_2\text{O}_3/\text{GH}$ electrode. Fig. 7a shows the survey spectra of $\text{Fe}_2\text{O}_3/\text{GH}$ electrodes of fresh (black line) and discharge to -1.0 V (red line). It was clearly observed that $\text{Mg } 1s$, $\text{Mg } 2s$, and $\text{Mg } 2p$ are discovered in the discharge to -1.0 V , and the $\text{F } 1s$ peak comes from PVDF and $\text{C } 1s$ peak

from acetylene black and graphene. Fig. 7b depicts the $\text{C } 1s$ XPS spectra can be divided into four peaks, centered at 284.0, 285.4, 288.3 and 291.8 eV, respectively. They are consistent with the references of $\text{C}=\text{C}$, $\text{C}-\text{O}$, sp^2 -bonded C atoms and CF. The corresponding fraction of $\text{C}=\text{C}$ bonding was almost the highest, revealing a deep deoxidation of graphene oxide. The CF comes from PVDF. As shown in Fig. 7c, the characteristic peaks in $\text{O } 1s$ XPS spectra can be divided into three peaks. The peak at a binding energy of

529.0 eV represents an anion O²⁻ for Fe₂O₃ in the center. Another peak at 531.2 eV indicates the presence of non-hydroxyl equivalent (or chemically adsorbed water) and Fe₂O₃ on the surface of the oxygen ion in the anoxic zone, and the third peak at 532.8 eV is corresponding to C=O in GH. Fig. 7d shows the Mg 1s peak is located at 1303 eV for the reduced electrode that discharges to -1.0 V. It is proved that a large number of Mg²⁺ ions are inserted into the lattice

of the Fe₂O₃/GH electrode after the discharge process. In Fig. 7e, the electrode was observed in fresh Fe 2p XPS spectra with two peaks at 725.4 and 711.4 eV. This electrode is not inserted into Fe₂O₃/GH for magnesium ions^[17, 36] and in good agreement with the formation of Fe₂O₃. When the electrode discharges to -1.0 V, the weak Fe 2p_{3/2} and Fe 2p_{1/2} peaks at 719.0 eV correspond to the characteristic peaks and their shake-up satellite peak of Fe 2p, respectively.

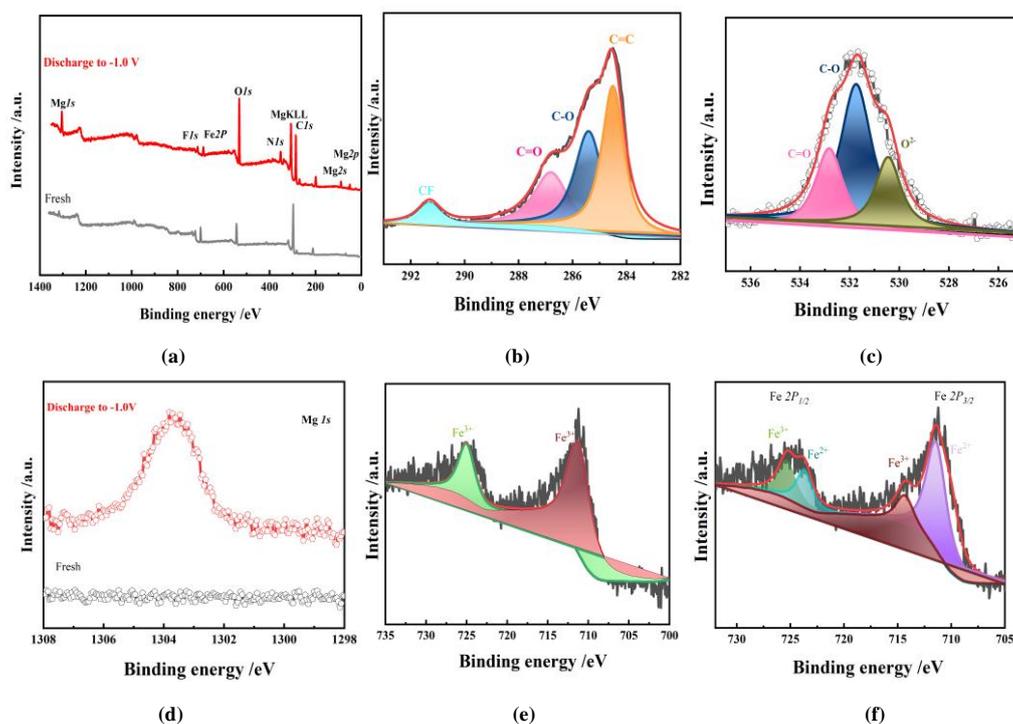


Fig. 7. XPS spectra of the fresh Fe₂O₃/GH and discharge to -1.0 V electrodes (a) and C 1s core level spectra of fresh (b), O 1s core level spectra of fresh (c), and Mg 1s core level spectra (d), Fe 2p core level spectra of fresh (e) and discharge to -1.0 V electrode (f)

4 CONCLUSION

In this work, we introduced an anodic electrode of Fe₂O₃ in aqueous MIBs and recombined it with graphene hydrogels (GH) to form Fe₂O₃/GH. The Fe₂O₃ and Fe₂O₃/GH were electrochemically measured in different aqueous solutions. The Fe₂O₃ and Fe₂O₃/GH electrodes have overcome some problems such as the conservation of cycle stability and efficiency. The Fe₂O₃/GH as anode exhibits a high specific rate capacity and rate ability in 0.5 M MgSO₄ + FeSO₄. The charge/discharge specific capacity approaches to 86%

capacity retention after 200 cycles, and the Fe₂O₃/GH electrode delivers a reversible capacity of 155 mAh g⁻¹ at 100 mA g⁻¹ with the coulombic efficiency close to 100%. Even at a high current density of 1000 mA g⁻¹, all electrochemical platforms remain unchanged, and the discharge specific capacity is 25 mAh g⁻¹. This material has not only a long cycle characteristic but also stable Coulomb efficiency, thus playing an important role in the construction of our green energy. For fixed or grid-level energy storage applications, it would be a viable alternative.

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