FeO$_x$-Based Materials for Electrochemical Energy Storage

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Iron oxides (FeO$_x$), such as Fe$_2$O$_3$ and Fe$_3$O$_4$ materials, have attracted much attention because of their rich abundance, low cost, and environmental friendliness. However, FeO$_x$, which is similar to most transition metal oxides, possesses a poor rate capability and cycling life. Thus, FeO$_x$-based materials consisting of FeO$_x$, carbon, and metal-based materials have been widely explored. This article mainly discusses FeO$_x$-based materials (Fe$_2$O$_3$ and Fe$_3$O$_4$) for electrochemical energy storage applications, including supercapacitors and rechargeable batteries (e.g., lithium-ion batteries and sodium-ion batteries). Furthermore, future perspectives and challenges of FeO$_x$-based materials for electrochemical energy storage are briefly discussed.

1. Introduction

Currently, with the rapid development of the economy, the overconsumption of fossil fuels has resulted in great demand for energy. As a consequence, a sustainable and low-cost way to store energy more efficiently has been continuously explored in recent years, especially for studies on electrochemical energy storage. Green electrochemical energy storage devices mainly include supercapacitors (SCs) and rechargeable batteries (lithium-ion batteries (LIBs), sodium-ion batteries (SIBs), lithium–sodium ion batteries (LSBs), and so on).

Iron (Fe) is the fourth richest element on earth, forming much of Earth’s outer and inner core. Fe$_x$ materials, including FeO, Fe$_2$O$_3$, and Fe$_3$O$_4$, are extensively used in industrial production for products used in daily life. Due to their high theoretical capacity of 800–1000 mA h g$^{-1}$, Fe$_2$O$_3$ and Fe$_3$O$_4$ have received much attention. In addition, FeO$_x$-based materials, other metal oxide materials, and carbon materials have been widely reported for applications in electrochemical energy storage, which can effectively reduce the obvious volume change that results in capacity decay and poor performance.

Considerable work of nanostructured Fe-based and FeO$_x$-based materials has been reported. Fe-based materials including Fe$_3$O$_4$, CoFe$_2$O$_4$, FeOOH, FeO$_x$, and MnFe$_2$O$_4$ were investigated by Zeng et al. when applied as electrodes for SIBs. Zhang et al. reviewed FeO$_x$-based materials (Fe$_2$O$_3$, Fe$_3$O$_4$ in LIBs based on 1D nanowires (NWs)/rods, 2D nanosheets/flakes, 3D porous/hierarchical architectures, various hollow structures, and hybrid nanostructures of Fe$_2$O$_3$ and carbon (including amorphous carbon, carbon nanotubes, and graphene), the nanostructures and electrochemical performance of which are also presented. The morphology, composition, porosity, and surface characteristics all affect the performance of FeO$_x$-based materials. Literature progress of FeO$_x$-based materials for SCs, LIBs, SIBs, and other batteries has been demonstrated, as shown in Figure 1a,b. Therefore, it is necessary to provide a review of FeO$_x$-based materials for applications in electrochemical energy storage.

In this review, we focus on the FeO$_x$-based materials for applications in electrochemical energy storage, including SCs and rechargeable batteries (LIBs, SIBs, LSBs, and so on). The comparison of FeO$_x$-based materials is on Table 1. Generally, Fe$_2$O$_3$ and Fe$_3$O$_4$ have been combined with metal-based materials and carbon materials, such as carbon nanotubes (CNTs) and graphene. In addition, their synthesis, structure, and electrochemical performance are discussed as well. Finally, future perspectives and challenges of FeO$_x$-based materials for electrochemical energy storage are briefly presented.

2. Crystal Structures and Charge Storage Mechanism

To explore better performances for the applications in electrochemical energy storage, the charge storage mechanism and the effect of crystal structures on the electrochemical performances should be studied.

On the basis of the charge storage mechanisms, SCs can be divided into electrical double-layer capacitors (EDLCs) and pseudocapacitors. The charge storages of them all occur at the surface or in the thin layer parts of active materials. The former focuses on charge separation and accumulation, while the latter are based on reversible and fast redox reactions. Pseudocapacitors have attracted more attention owing to the higher energy density compared to that of EDLCs. On the one hand, FeO$_x$ are widely used in pseudocapacitors due to the various valence states (Fe$^0$, Fe$^{2+}$, Fe$^{3+}$, and so on) and unique crystal structures of their ions, which ensure the occurrence of reversible
and fast redox reactions. Fe₃O₄ generally has three crystal structures, including α-Fe₂O₃, β-Fe₂O₃, γ-Fe₂O₃. β-Fe₂O₃ and γ-Fe₂O₃ are the transition states for the evolution to α-Fe₂O₃. Meanwhile, the crystal structure of α-Fe₂O₃ is more stable than that of β-Fe₂O₃ and γ-Fe₂O₃, which ensures the long life for SCs (Figure 2).[1] In addition, more conductive materials, including carbon-based materials, conductive polymer, and metal materials, can be combined with FeOₓ in order to improve the conductivity (Figure 3). Besides, desirable structures are designed to increase the surface area and improve the stability.

Meanwhile, the charge mechanism of rechargeable batteries is related with fast transfer of Li⁺. It is crucial to shorten the path length for transport of Li⁺ and ensure the absorption and storage of large amount of Li⁺ without causing deterioration. The theoretical capacitances of FeO, α-Fe₂O₃, and Fe₃O₄ are about 600, 1000, and 800 mA h g⁻¹, respectively. In addition, better conductivity and more desirable morphologies have a good influence on the transition, absorption, and storage of large amount of lithium ions without causing deterioration. The transfer of Li⁺ can occur on the surface and in most of the active materials. Take LIBs as an example, the electrochemical reactions of FeOₓ are presented, respectively

\[
\text{FeO: } \text{FeO} + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{FeO}
\]

\[
\text{Li}_x\text{FeO} + (2 - x) \text{Li}^+ + (2 - x)e^- \rightarrow \text{Li}_2\text{O} + \text{Fe}
\]  \quad (1)

\[
\text{Fe}_2\text{O}_3: \text{Fe}_2\text{O}_3 + 6\text{Li}^+ + 6e^- \rightarrow 2\text{FeO} + 3\text{Li}_2\text{O}
\]  \quad (2)

\[
\text{Fe}_3\text{O}_4: \text{Fe}_3\text{O}_4 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{Fe}_3\text{O}_4 \\
\text{Li}_x\text{Fe}_3\text{O}_4 + (8 - x)\text{Li}^+ + (8 - x)e^- \rightarrow 4\text{Li}_2\text{O} + 3\text{Fe}
\]  \quad (3)

Generally, major efforts have been made, as shown in Figure 3, in order to achieve enhanced performances not only in SCs but also in LIBs. The problems of poor conductivity and large volume change can be largely diminished so that the FeOₓ-based materials with enhanced stability will be examined as promising anode electrode materials in rechargeable batteries, especially high performance LIBs.

Table 1. The comparison of FeOₓ-based materials for applications in energy storage.

| Materials | FeO-based materials | Fe₂O₃-based materials | Fe₃O₄-based materials |
|-----------|---------------------|-----------------------|----------------------|
| Synthesis | Hard to obtain, unstable | Easier to obtain than others (hydrothermal method) | Complicated synthetic process |
| Morphology | Nanoparticles, nanowires | Nanoparticles, nanospindles, microspheres, nanowires, nanorods, nanocubes, films, and so on | Nanoparticles, nanospindles, nanofibers, films, nanospheres, nanowires, nanorods, and so on |

**Performance in LIBs**

| Voltage range | 0–3 V | 0–3 V | 0–3 V |
|---------------|-------|-------|-------|
| Reversible capacity | 600–800 mA h g⁻¹, 0.1–1 A g⁻¹ | 600–1000 mA h g⁻¹, 0.5–1 A g⁻¹ | 900–1500 mA h g⁻¹, 1–10 A g⁻¹ |
| Cycle ability | 95–100%, 50–100 cycles | 55–99%, 50–500 cycles | 50–95%, 50–200 cycles |
| Rate capability | 500–600 mA h g⁻¹, 0.5–1 A g⁻¹ | 900–1300 mA h g⁻¹, 0.1–1 A g⁻¹ | 900–1400 mA h g⁻¹, 1–9 A g⁻¹ |

**Performance in SCs**

| Specific capacitance | 500–1000 F g⁻¹, 1–2 A g⁻¹ | 150–300 F g⁻¹, 1–10 A g⁻¹ | 100–200 F g⁻¹, 0.5–10 A g⁻¹ |
| Energy density | 20–50 Wh kg⁻¹ | 40–80 Wh kg⁻¹ | 30–60 Wh kg⁻¹ |

**Suitable applications**

SCs | LIBs | LIBs

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3. Fe₂O₃-Based Nanomaterials

In the modern society, Fe₂O₃ materials play an important role in electrochemical energy storage systems. Due to its abundance, environmental friendliness, good electrochemical activity, high stability under ambient conditions, and low cost, Fe₂O₃ has attracted much attention as a negative electrode material in electrochemical energy storage.

3.1. Supercapacitors

According to the energy storage mechanisms, SCs can be divided into EDLCs, pseudocapacitors, and hybrid capacitors. Moreover, the electrochemical performance of Fe₂O₃-based materials for SCs depends mainly on the structure and test conditions, including the electrolyte, applied mass loading voltage and electrode configuration, or device assembly. Here, we focus on the material selection, synthesis, structure, and electrochemical performance. Currently, FeOₓ, along with metals, other MOₓ, and carbon materials, have been studied and widely reported. Exploring novel FeOₓ-based materials with desirable structures is an effective way to further improve the electrochemical performance of SCs.

3.1.1. Pure Fe₂O₃

Pure Fe₂O₃ nanoparticles (NPs), films, nanosheets, and hollow nanoshuttles have been widely explored for applications in SCs.

Generally, strategies for the synthesis of pure Fe₂O₃ mainly include the electrosprinning, template, and hydrothermal methods. Binitha et al. fabricated two different morphologies of α-Fe₂O₃, nanograin (NG), and porous fiber (PF), using the electrosprinning method to obtain α-Fe₂O₃ particles of 21 and 53 nm in size, respectively. Ferric acetyl acetonate (Fe(acac)₃), which was used as an α-Fe₂O₃ precursor together with Fe₂O₃-polyvinyl pyrrolidone (PVP)/polyvinyl acetate (PVAc) fibers, was used for the synthesis of α-Fe₂O₃ PFs and...
NGs (Figure 4f,g). In addition, the evolution of the structure contributed to the chemical interactions between the Fe(acac)₃ and polymer, as shown in Figure 4a. The α-Fe₂O₃ PFs delivered a specific capacitance and a power density of 348 F g⁻¹ and 1149 W kg⁻¹ at 5 A g⁻¹, respectively, which were higher than those of the α-Fe₂O₃ NGs (159 F g⁻¹ and 997 W kg⁻¹). In addition, the as-obtained materials also exhibited superb cycling performance (256 F g⁻¹ at 1 mV s⁻¹). Additionally, flexible SCs were obtained by Nan et al. by fabricating porous spinous Fe₂O₃ materials (PSI) on a thin Fe substrate with superior flexibility (Figure 4b) via a template method. [33] Figure 4d,e shows the as-prepared products with 20–50 nm in width and 200–400 nm in length after heat treating at 400 °C for 4 h. It was demonstrated that the as-prepared SCs maintained a good current at different curvatures due to the flexibility of the Fe substrate (Figure 4j). As a result, PSI displayed specific capacitances of 524.6, 362.5, and 313.1 F g⁻¹ at 1, 10, and 20 A g⁻¹, respectively, and showed superior cycling stability (92.9% of the initial value) over 5000 cycles. In conclusion, the fiber-based all-solid-state flexible SCs (Figure 4h) successfully illuminated an LED (Figure 4c). Furthermore, a hydrothermal method was used by Zheng et al. for the fabrication of α-Fe₂O₃ hollow nanoshuttles with a uniform wall thickness of 30 nm and a length of 100 nm. [31] Figure 4i shows that the charge transfer resistances of 4.42, 4.12, and 3.80 Ω were achieved at 20, 40, and 60 °C, respectively, and the α-Fe₂O₃ hollow nanoshuttles displayed an excellent capacitance of 249 F g⁻¹ at 0.5 A g⁻¹.

![Figure 2. Crystal structures of α-, β-, γ-Fe₂O₃, FeO, and Fe₃O₄ (yellow globule: Fe²⁺/Fe³⁺ Red globule: Fe³⁺).](image-url)

![Figure 3. The schematic illustration of pure FeOₓ and FeOₓ-based composites including the factors of electrochemical performances.](image-url)
3.1.2. Fe₂O₃/Carbon Nanomaterials

Fe₂O₃ combined with carbon materials, such as CNTs and graphene, have been reported as anodes for application in SCs. The porous α-Fe₂O₃/CNTs hierarchical nanostructure[34] and Fe₂O₃/multiwall carbon nanotubes (MWCNTs) thin films[35,36] have been studied. The α-Fe₂O₃/MWCNTs materials synthesized by Zhao et al. via a scalable spray deposition method displayed a high power density of 50 W h kg⁻¹ for hybrid SCs at 1000 W kg⁻¹.[36] Nanoporous Fe₂O₃ with 5 wt% CNT materials, which were prepared by Xu et al. using scanning-mode N₂ atmospheric pressure plasma jets, displayed a specific capacitance of 54 F g⁻¹ at 2 mV s⁻¹.[37] Cheng et al. coated Fe₂O₃ nanohorns with a conductive CNT network using the chemical vapor deposition (CVD) method.[34] The as-fabricated materials delivered a maximum capacitance of 296.3 F g⁻¹ at 5 mV s⁻¹ and remained at 80% and 60% of the initial capacitance over 200 and 1000 cycles, respectively. Furthermore, a specific capacitance of 296.3 F g⁻¹ was obtained by the Fe₂O₃/CNTs sponge over 1000 cycles of compression under 50% strain, demonstrating great potential in flexible energy storage devices.

In addition to Fe₂O₃/CNTs composites, Fe₂O₃/graphene composites, such as Fe₂O₃/graphene aerogel (GA) composites[38,39] and Fe₂O₃ nanoplates/graphene,[40] have been explored mainly through hydrothermal/solvothermal method. The Fe₂O₃ NPs with the sizes of 30–60 nm encapsulated in GA were synthesized by Song et al., which displayed a specific capacitance of 81.3 F g⁻¹ at 1 A g⁻¹.[39] Similarly, Fe₂O₃/GA materials were also fabricated by Khatkak et al., and they delivered a specific capacitance of 440 F g⁻¹ at 0.45 A g⁻¹.[38] Furthermore, the as-obtained materials maintained 90% of their initial capacitance, even after 2200 cycles. Apart from the Fe₂O₃/GA materials, α-Fe₂O₃ nanoplates connected with reduced graphene oxide (rGO) network materials were prepared by Quan et al. using a hydrothermal method.[41] A specific capacitance of 903 F g⁻¹ at 1 A g⁻¹ was achieved for the α-Fe₂O₃/rGO materials, which was higher compared to that of pure Fe₂O₃ (347 F g⁻¹).

Furthermore, Fe₂O₃ NP clusters/rGO was synthesized by Hu et al. via gel formation reaction, hydrothermal process, vacuum filtration, and electrochemical reduction four procedures for applications in flexible asymmetric supercapacitors, which are of great potential for electrochemical energy storage owing to the superior energy density.[42] The rGO sheets ensured the superior conductivity and flexibility while the Fe₂O₃ NP clusters had satisfactory performances for pseudocapacitors without weakening the high conductivity of the overall hybrid paper so that a high energy density of ≈74.7 Wh kg⁻¹ at a ≈1400 W kg⁻¹ and a capacitance retention of ≈95.4% over 50 000 cycling tests were achieved.
3.1.3. Fe₂O₃/Metal-Based Nanomaterials

Fe₂O₃-MOₓ materials, such as CeO₂/Fe₂O₃ composite nanosphindles (CNSs), V₂O₅/α-Fe₂O₃ nanotubes, Fe₂O₃/CuO thin films, NiO nanosheets/Fe₂O₃ nanorods (NRSs) and RuO₂/Fe₂O₃ NPs, have also been applied in the SCs.

Arul et al. fabricated CNSs with a crystallite size of 4.47 nm, and the size was the smallest among CeO₂ NPs (15.75 nm) and Fe₂O₃ NRSs (4.62 nm) using a coprecipitation method. In addition, a specific capacitance of 142.6 F g⁻¹ at 5 mV s⁻¹ and an outstanding capacitance retention of 94.8% at the 1000th cycle were achieved, demonstrating great potential for applications in SCs. Additionally, V₂O₅-decorated α-Fe₂O₃ nanotubes were fabricated by Nie et al. using an electrospinning approach. The V₂O₅/Fe₂O₃ materials with weight ratios of 0%, 1.0%, 2.5%, 5.0%, and 10.0% were named VFNT0, VFNT1, VFNT2, VFNT3, and VFNT4, respectively. The VFNT1 materials with a diameter of 117 nm delivered a specific capacitance of 183 F g⁻¹ at 1 A g⁻¹, which was higher than that of VFNT0 (100.5 F g⁻¹). In addition, an areal capacitance was achieved retaining more than 60% even at 5 A g⁻¹. Furthermore, Jiao et al. fabricated α-Fe₂O₃ NPs/NiO nanosheets 30 nm in diameter and 300 nm in length via a hydrothermal method, and they displayed a superb areal capacitance of 557 mF cm⁻². Moreover, a specific capacitance retention of ≈96.2% was obtained over 3000 cycles at 1 mA cm⁻², providing great potential for applications in SCs.

3.2. LiBs

Motivated by the demand for portable electronic devices and electric vehicles, rechargeable LiBs have been developed over the last few decades and have attracted increasing attention. Currently, they demonstrate barriers to realization using commercial graphite anodes because of the low lithium-ion storage capacity (372 mA h g⁻¹). To improve the energy density of batteries, various promising materials with high theoretical capacities have been used. In addition, many significant studies have been conducted in recent decades to develop the electrochemical energy storage of LiBs.

3.2.1. Pure Fe₂O₃

Pure Fe₂O₃ is mainly obtained by the spray pyrolysis method and electrospinning-annealing method. Xu et al. synthesized γ-Fe₂O₃ with a crystalline structure of ≈1 μm in diameter and a pore size of 0.4 μm through aerosol spray pyrolysis at different temperatures. The γ-Fe₂O₃ spherical particles exhibited a specific capacity of 800 mA h g⁻¹ at 0.5 C after 300 cycles and remained at 300 mA h g⁻¹ at 10 C. Jiang et al. synthesized hierarchically porous Fe₂O₃, which exhibited initial discharge/charge capacities of 1658 and 1130 mA h g⁻¹ and an outstanding cyclability of 1600 mA h g⁻¹ after 500 cycles at 1 A g⁻¹. Furthermore, Cherian et al. prepared α-Fe₂O₃ NRs with an average diameter of 150 nm via an electrospinning and annealing approach using PVP/ferric acetyl acetonate (Fe(acac)₃) precursors. The materials displayed a charge capacity of 1109 and 1095 mA h g⁻¹ during the 1st and 2nd cycles, respectively. In addition, the reversible capacity decreased at high rates and achieved a value of 1090 mA h g⁻¹ after 70 cycles (Figure 5j,k).

3.2.2. Fe₂O₃/Carbon Nanomaterials

In addition to graphene and CNTs, FeOₓ can also form a compound with carbon. Thus, Fe₂O₃ NPs/carbon materials and α-Fe₂O₃ core–shell nanorings and nanocrystalline α-Fe₂O₃-loaded carbon have been studied as well.

A hydrothermal method can be used for the synthesis of Fe₂O₃/carbon NRs and α-Fe₂O₃/carbon nanorings. Wang et al. fabricated Fe₂O₃/carbon NRs on carbon cloth via a hydrothermal approach; the first step involved loading the Fe₂O₃ NR arrays, and the second step involved carbon coating (Figure 6a). The Fe₂O₃/carbon materials (Figure 6e,f) delivered initial discharge/charge capacities of 2912.6 and 2283.9 mA h g⁻¹. Li et al. fabricated α-Fe₂O₃/carbon nanorings with an outer diameter of 148 nm, a thickness of 50 nm, and a length of 115 nm using a hydrothermal method, and this was followed by a carbon-coating process to form rings enwrapped with a carbon shell = 3 nm in thickness (Figure 6g,h). This material demonstrated a specific capacity of 815 mA h g⁻¹ at 1000 mA h g⁻¹ over 160 cycles.

Other methods, which include the template method and modified coprecipitation method in situ carbonization method, have also been used for the fabrication of Fe₂O₃/carbon materials. Hu et al. successfully synthesized ordered mesoporous carbon nanowire (OMCNW)/Fe₂O₃ materials with a template method (Figure 6b). Three kinds of ordered mesoporous carbons (OMCs), namely, FDU-15, CMK-8, and OMCNW, were fabricated with disordered porous carbon nanowires (DPCNWs) via the soft-template, hard-template, and soft-hard dual-template methods, respectively. The OMCNWs displayed the first lithiation/delithiation capacities of 1621 and 650 mA h g⁻¹ and a lithiation capacity of 698 mA h g⁻¹ during the 2nd cycle, which is higher than that of graphite (Figure 6i,j). Oh et al. fabricated Fe₂O₃/carbon materials using a modified coprecipitation method and found that...
the Fe₂O₃/carbon materials displayed a discharge capacity of 1094 mA h g⁻¹ during the 1st cycle (Figure 6k,l). In addition, the electrode exhibited an initial charge capacity of 815 mA h g⁻¹ at 0.1 C, and the capacity retention improved by 150%. Cheng et al. prepared α-Fe₂O₃/carbon nanocomposites 30–35 nm in size using an in situ carbonization approach. The oleic acid-capped α-Fe₂O₃ NPs, which were applied as the precursor, were annealed at 300 °C for 2 h to prepare the α-Fe₂O₃/carbon materials. As a result, the as-prepared Fe₂O₃/carbon materials exhibited superb conductivity and good cycling stability. In addition, a chemical vapor deposition method was also used for the synthesis of Fe₂O₃ NPs/GF by Guan et al. and discharge capacities of 514.0 and 214.3 mA h g⁻¹ at 5 A g⁻¹ and 30 A g⁻¹ were obtained, respectively. A capacity retention of 95.8% was achieved at 30 A g⁻¹ after 400 cycles as well. In a nutshell, the carbon-based materials have improved the conductivity of the compounds so that better performances have been achieved in LIBs.

Fe₂O₃ nanobelts/CNTs, Fe₂O₃ NPs/CNT film materials, and other morphologies have been synthesized as well. A single-walled Fe₂O₃/carbon nanotube (SWCNT) membrane was prepared by Zhou et al. with 88.0 wt% Fe₂O₃ NPs (5–10 nm) using floating catalyst CVD (Figure 7a); the first discharge/charge capacities of the Fe₂O₃/SWCNT membrane were 2097 and 1243 mA h g⁻¹, respectively, which were higher than those of the SWCNT membrane (Figure 7j). Furthermore, a superior reversible capacity of ≈1200 mA h g⁻¹ was obtained by the Fe₂O₃/SWCNT membrane at 50 mA g⁻¹, and the materials maintained specific capacities of 750 and 405 mA h g⁻¹ even at 1000 and 2500 mA g⁻¹, respectively, which were much better than that of SWCNTs (124 and 80 mA h g⁻¹). Besides, γ-Fe₂O₃/MWCNTs with a spider-web-like structure were fabricated by Bhattacharya et al. via an ozonation–templating–heating method (Figure 7b). The as-prepared MWCNT/γ-Fe₂O₃ (MWF) materials were designated as MWF0.1, MWF1, and MWF2 for the ratios of 24.05, 45.15, and 65.65 wt%, respectively. Among them, MWF1, with IR signatures of 490–800 cm⁻¹, exhibited the best capacity of 766 mA h g⁻¹ compared to those of MWF0.1 and MWF2 achieving 609 and
196 mA h g⁻¹ at 0.1 A g⁻¹, respectively (Figure 7k). It was also demonstrated that a superb discharge capacity of ≈822 mA h g⁻¹ at 0.05 A g⁻¹, a retention of ≈72.3% between 0.05 to 1 A g⁻¹, and an outstanding cycling stability of >88% over 310 cycles (coulombic efficiency >99%) were achieved with these materials.

Apart from above studies, Gu et al. fabricated branched core–shell Fe₂O₃/carbon materials (Figure 7d) with different types of Fe₂O₃/CNT materials via a hydrothermal approach, and they were named samples I, II, and III. [74] The three kinds of samples were wrapped with thicknesses of 0.9, 2.5, and 3.9 nm, respectively. The results show that sample I, having the thinnest carbon layer, performed best among all the as-obtained materials and delivered high capacities of 1173 and 1014 mA h g⁻¹ at 0.2 and 1 A g⁻¹, respectively, over 100 cycles, while those of the other two samples were only 1025 mA h g⁻¹ and 820 mA h g⁻¹, 815 mA h g⁻¹ and 680 mA h g⁻¹. Moreover, sample I exhibited coulombic efficiencies of ≈73% and displayed a reversible capacity of 482 mA h g⁻¹ at 4 A g⁻¹ even over 1000 cycles. Wu et al. synthesized Fe₂O₃ nanobelt/CNT materials 10 nm in width by the precipitation of FeC₂O₄ on CNTs and a heat-treatment process (Figure 7h,i). [70] The Fe₂O₃ nanobelt/CNT materials delivered initial discharge/charge capacities of 1191.4 and 847.5 mA h g⁻¹ at 100 mA g⁻¹ and a reversible capacity of 865.9 mA h g⁻¹ over 50 cycles and 442.1 mA h g⁻¹ at 4 A g⁻¹. Sun et al. fabricated Fe₂O₃/CNT materials containing 44.8% Fe₂O₃ (M-400) through an ammonia hydrolysis and pyrolysis two-step process. [75] A charge capacity of 619 mA h g⁻¹ was obtained by M-400 materials over 80 cycles at 50 mA g⁻¹, which achieved a superior charge capacity retention of 94.9% and even maintained 376 mA h g⁻¹ at 500 mA g⁻¹ (Figure 7l). Overall, the electrochemical performance of the Fe₂O₃/CNT materials is better than that of pure Fe₂O₃ for applications in energy storage devices.

A hydrothermal method [76] and sol–gel process [77] can be used for the synthesis of Fe₂O₃/carbon aerogel (CA) materials. Luo et al. fabricated α-Fe₂O₃/CA materials with a size of 34 nm
(Figure 7e–g) through the hydrothermal process in an aqueous solution, which performed best among all the other as-prepared materials of different sizes (Figure 7c). The $\alpha$-Fe$_2$O$_3$/CA materials delivered a specific capacity of 581.9 mA h g$^{-1}$ at 100 mA g$^{-1}$ over 50 cycling tests and a reversible capacity of 512.3 mA h g$^{-1}$ even at 1000 mA g$^{-1}$ (Figure 7m). Furthermore, Liu et al. fabricated Fe$_2$O$_3$ NPs/CA materials via a sol–gel process by soaking in a solution of Fe(NO$_3$)$_3$ and continuous annealing. The Fe$_2$O$_3$/CA-60 materials (carbon:Fe$_2$O$_3$ = 48.8%:32.0%) displayed reversible capacities of 881 and 546 mA h g$^{-1}$ at 100 and 800 mA g$^{-1}$. Furthermore, the initial charge/discharge capacities of 916, 521 mA h g$^{-1}$ were obtained by the as-prepared materials, and the initial charge capacity of the as-prepared materials was higher than those of Fe$_2$O$_3$ (816 mA h g$^{-1}$) and CA (487 mA h g$^{-1}$); however, there was no obvious change in the initial discharge capacity. It turned out that the carbon aerogel assisted the anode materials in achieving a good capacity retention, which effectively promoted their good performance in LIBs.

A precipitation method, a hydrothermal method, and an electrospinning method have also been explored to synthesize Fe$_2$O$_3$ NRs/carbon nanofibers (CNFs). Park et al. fabricated Fe$_2$O$_3$ NR/CNF materials with a diameter of 14 mm via a precipitation approach. The scanning electron microscope (SEM) images of the bare CNFs and the Fe$_2$O$_3$/CNF composites with a scale bar of 200 nm are shown in Figure 8a–d. The Fe$_2$O$_3$/CNF materials delivered a specific capacity of 515.1 mA h g$^{-1}$ at 0.5 A g$^{-1}$, which was higher than not only the pure Fe$_2$O$_3$ NPs of 125.3 mA h g$^{-1}$ but also the pure CNFs of 153.2 mA h g$^{-1}$ (Figure 8k,l). Wu et al. synthesized $\alpha$-Fe$_2$O$_3$ NR/carbon materials (Figure 8g–j) with $\alpha$-Fe$_2$O$_3$ NRs 75 nm in diameter and 1 $\mu$m in length that were coated with CNFs via a hydrothermal method (Figure 8e).[79] The as-obtained materials delivered an initial discharge capacity of 1278 mA h g$^{-1}$ at 0.2 C and maintained 960 mA h g$^{-1}$ over 30 cycles, demonstrating better performance than pure $\alpha$-Fe$_2$O$_3$ NRs. Cho et al. prepared Fe$_2$O$_3$/carbon nanofibers with a bubble-nanorod structure using an electrospinning method, and the hollow nanospheres exhibited a size of 17 nm and a thickness of 3 nm (Figure 8f).[80] As a result, the pure Fe$_2$O$_3$ displayed initial discharge/charge capacities of 1406 and 1145 mA h g$^{-1}$, while the as-prepared materials were only 1385 and 975 mA h g$^{-1}$, and in the long-term, the
capacity loss of pure Fe₂O₃ was greater than that of the Fe₂O₃/carbon nanofibers after several cycles. For example, the as-prepared materials delivered a discharge capacity of 812 mA h g⁻¹ after 300 cycles, which was higher than that of the pure Fe₂O₃ nanofibers (284 mA h g⁻¹). In addition, the retention of each was 84 and 24%, respectively, during the 2nd cycle.

Fe₂O₃ NPs/graphene,[81] Fe₂O₃/graphene hierarchical nanospheres,[82] Fe₂O₃ nanocrystals wrapped in graphene,[83] and core–shell nanohollow Fe₂O₃/graphene[84] have also been applied in LIBs for good electrochemical performance. Different methods, such as the adsorption–precipitation method,[85] hydrothermal method,[86] and in situ CVD method,[87] have been used for the fabrication of Fe₂O₃/graphene materials. Zhu et al. prepared Fe₂O₃/nanomesh graphene (NMG) materials by an adsorption and precipitation two-step process (Figure 9a).[85] Reversible capacities of 1567 mA h g⁻¹ at 150 mA g⁻¹ for 50 cycles and 883 mA h g⁻¹ at 1000 mA g⁻¹ for 100 cycles were displayed by Fe₂O₃/NMG materials. Differently, Meng et al. fabricated an α-Fe₂O₃ NPs/GA via a hydrothermal method (Figure 9b), which demonstrated a surface area of 212.5 m² g⁻¹ and a pore volume of 0.2073 cm³ g⁻¹.[86] Moreover, the α-Fe₂O₃ NPs/GA materials showed discharge capacities of 691.9 and 187.1 mA h g⁻¹ at 100 and 2000 mA g⁻¹, which were higher than those of the pure Fe₂O₃ (358.2 and 4.4 mA h g⁻¹, respectively). An in situ CVD method was used by Zhang et al. for the synthesis of yolk–shell γ-Fe₂O₃ NPs encapsulated with graphene shells (YS-g-Fe₂O₃@G-GS) (Figure 9c).[87] The as-prepared materials showed good cycling stability (663.7 mA h g⁻¹ at 2 A g⁻¹), superb rate capability (1173, 989, 827, 737, 574, 443, and 350 mA h g⁻¹ at 0.1, 0.2, 0.5, 1, 2, 5, and 10 C, respectively) with a retention of ≈96.6% over 1500 cycles (Figure 9k).

In addition, Jiang et al. obtained 3D graphene/Fe₂O₃ materials (Figure 9d) through a combined metal-ion-induced spatially confined Ostwald ripening method.[88] As shown in Figure 9g, the 3D graphene/Fe₂O₃ materials demonstrated flexibility; therefore, the films were compressed from ≈4 mm to ≈50 μm in thickness. The as-fabricated materials delivered...
a discharge capacity of 1129 mA h g\(^{-1}\) at 0.2 A g\(^{-1}\) over 130 cycling tests and exhibited excellent cycling stability retaining 98% of the initial value over 1200 cycling tests at 5 A g\(^{-1}\). Wang et al. prepared Fe\(_2\)O\(_3\) (1 nm in size) dropped with GNSs (30 nm in size) through a dielectric barrier discharge plasma assisted milling (P-milling).

Wang et al. prepared Fe\(_2\)O\(_3\) (1 nm in size) dropped with GNSs (30 nm in size) through a dielectric barrier discharge plasma assisted milling (P-milling). It was demonstrated that the initial discharge capacities of 851 mA h g\(^{-1}\) at 100 mA h g\(^{-1}\) over 5 cycles were obtained for these materials (Figure 9j). Chen et al. synthesized \(\alpha\)-Fe\(_2\)O\(_3\) NRs dropped with a CNTs/GF, which showed good conductivity (Figure 9e,f). The materials displayed initial discharge/charge capacities of 1310 and 1028 mA h g\(^{-1}\) and, furthermore, exhibited 500 mA h g\(^{-1}\) at 3000 mA g\(^{-1}\) (Figure 9h,i). In conclusion, \(\alpha\)-Fe\(_2\)O\(_3\)/CNT/GF composites are good anode materials that can be largely applied in LIBs.

Generally speaking, the methods for the synthesis of Fe\(_2\)O\(_3\)-rGO materials mainly include the precipitation–reduction method\(^{91}\) and the hydrothermal method\(^{92,93}\). Zhu et al. fabricated Fe\(_2\)O\(_3\)-rGO materials (the average diameter of the Fe\(_2\)O\(_3\) particles is ~60 nm) through a precipitation and reduction two-step process (Figure 10a).\(^{91}\) Moreover, initial discharge/charge capacities of 1693 and 1227 mA h g\(^{-1}\) were achieved for the as-synthesized materials at 100 mA h g\(^{-1}\). In addition, the materials had a high capacity retention of 1027 mA h g\(^{-1}\) over 50 cycles, and the discharge capacity was maintained at ~800 mA h g\(^{-1}\) at 800 mA g\(^{-1}\) (Figure 10i,j). Xiao et al. synthesized Fe\(_2\)O\(_3\) NPs...
of 9 nm in diameter decorated on rGO sheets (Figure 10g,h) via a hydrothermal reduction process without any surfactant or chemical linker (Figure 10b).[92] Specific capacities of 600 and 180 mA h g\(^{-1}\) were achieved for the Fe\(_2\)O\(_3\)/rGO materials at 0.1 and 10 A g\(^{-1}\), respectively. Similarly, Chen et al. fabricated Fe\(_2\)O\(_3\) NPs (with an average size of \(\approx\) 180 nm) dropped on rGO sheets (Figure 10c,d) using a hydrothermal approach.[93] The initial discharge capacity of the Fe\(_2\)O\(_3\)/rGO material was 1186 mA h g\(^{-1}\), which was higher than pure Fe\(_2\)O\(_3\) with a specific discharge capacity of 1085 mA h g\(^{-1}\). In addition, the materials delivered a reversible capacity of 930 mA h g\(^{-1}\), while pure Fe\(_2\)O\(_3\) exhibited a reversible capacity of only 910 mA h g\(^{-1}\). This result is due to the rGO nanosheets promoting electron transport, improving the conductivity of the materials.

Based on above binary composites, ternary composites of carbon-wrapped Fe\(_2\)O\(_3\) particles deposited on graphene nanosheets (GNSs),[94] \(\alpha\)-Fe\(_2\)O\(_3\)/carbon/graphene microspheres,[95] and Fe\(_2\)O\(_3\)/graphene/CNT films[96] have been explored. Zhang et al. proposed a spray drying–carbonization–oxidation method to synthesize \(\alpha\)-Fe\(_2\)O\(_3\)/graphene/carbon microspheres with \(\alpha\)-Fe\(_2\)O\(_3\) NPs and graphitic carbon shells 30–50 nm in size and 5–10 nm in thickness.[95] The initial discharge/charge capacities of 1363 and 898 mA h g\(^{-1}\) were achieved at 400 mA g\(^{-1}\). In addition, the as-prepared materials exhibited a coulombic efficiency of 66% and even maintained 841 mA h g\(^{-1}\) over 100 cycles. Wang et al. prepared Fe\(_2\)O\(_3\)/carbon/GN materials, which were wrapped with a carbon layer with a thickness of 5 nm on Fe\(_2\)O\(_3\) particles 400 nm in size via a hydrothermal and glucose impregnation–pyrolysis two-step process.[94] The as-obtained materials exhibited the initial discharge/charge capacities of 1540 and 1100 mA h g\(^{-1}\) at 200 mA g\(^{-1}\), which were higher than those of pure Fe\(_2\)O\(_3\) (1288 and 706 mA h g\(^{-1}\)) and Fe\(_2\)O\(_3\)/GNSs (1475 and 936 mA h g\(^{-1}\)) and the coulombic efficiency of the materials was up 71%. Flexible Fe\(_2\)O\(_3\)/graphene/CNTs films with the hierarchical structure were fabricated by Wang et al. with pure Fe\(_2\)O\(_3\), which was 750 nm in diameter through filtration and reduction.

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two processes. As a result, the materials showed a reversible capacity of 716 mA h g\(^{-1}\) at 50 mA g\(^{-1}\) at the 120th cycle.\[96\]

### 3.2.3. Fe\(_2\)O\(_3\)/Metal-Based Nanomaterials

Apart from the Fe\(_2\)O\(_3\)/carbon materials, Fe\(_2\)O\(_3\)/metal-based materials such as \(\gamma\)Fe\(_2\)O\(_3\)/Ag NW nanocables\[97\] and \(\alpha\)Fe\(_2\)O\(_3\)/Li/Fe materials\[98\] have been studied. Geng et al. fabricated \(\gamma\)Fe\(_2\)O\(_3\)/Ag NW materials 90 nm in diameter through a mild oxidation method.\[97\] As a result, the materials exhibited a reversible capacity of 890 mA h g\(^{-1}\) over 60 cycling tests at 0.1 C and maintained 550 mA h g\(^{-1}\) even at 2.0 C. Differently, \(\alpha\)Fe\(_2\)O\(_3\) (with a crystallite size of 50 nm)/Li/Fe (with a crystallite size of 29 nm) materials were synthesized by Wang et al. through a gel polymer method.\[98\] The capacities of 1300 and 1400 mA h g\(^{-1}\) were obtained by \(\alpha\)Fe\(_2\)O\(_3\) and Li/Fe oxides, respectively, for which the initial capacitance loss resulted in a retention of only 21.8%.

Generally, Fe\(_2\)O\(_3\)/Co\(_3\)O\(_4\) materials can be synthesized by hydrothermal and hydrolysis methods\[99\] or annealing and chemical reactions.\[100\] Xiong et al. synthesized Fe\(_2\)O\(_3\)/Co\(_3\)O\(_4\) NW arrays with a nanocrystallite size of 10–20 nm and a pore size of 4–6 nm (Figure 11e,f) via hydrothermal and hydrolysis methods.\[101\] Figure 11b shows the growth of Co\(_3\)O\(_4\) nanowire arrays on a Ni substrate through a hydrothermal approach. The as-prepared materials displayed a cyclability of 1005.1 mA h g\(^{-1}\) over 50 cycling tests at 200 mA g\(^{-1}\) and a rate capacity of 788.9 mA h g\(^{-1}\) at 5000 mA g\(^{-1}\). \(\alpha\)Fe\(_2\)O\(_3\)/Co\(_3\)O\(_4\) branched NWs with 50–100 nm in diameter and length were prepared by Wu et al. via a hydrothermal approach, by which a first discharge capacity of \(\approx 1534\) mA h g\(^{-1}\) was achieved at 100 mA g\(^{-1}\), while those of the Co\(_3\)O\(_4\) NWs and \(\alpha\)Fe\(_2\)O\(_3\) were only 1188 and 155 mA h g\(^{-1}\), respectively.\[99\] Furthermore, the as-prepared materials maintained a reversible capacity of 980 mA h g\(^{-1}\) from the 2nd cycle to 60th cycle, which was higher than those of the Co\(_3\)O\(_4\) NWs (311 mA h g\(^{-1}\)) and \(\alpha\)Fe\(_2\)O\(_3\) NWs (75 mA h g\(^{-1}\)), and the capacitance retention was as high as 66% of the initial discharge capacity. Wang et al. fabricated Fe\(_2\)O\(_3\) NRs 10 nm in diameter on SnO\(_2\) nanosheets via a hydrothermal growth method.\[102\] The as-prepared materials exhibited a cyclability of 325 mA h g\(^{-1}\) over 50 cycles. Li et al. fabricated Fe\(_2\)O\(_3\)/Co\(_3\)O\(_4\) double-shelled hierarchical microcubes with an
800 nm average size by annealing Fe(FeCN)_{6}3J/Co(OH)_{2} microcubes and then reacting Co^{2+} (from Co(OH)_{2}) with OH⁻ (from the reaction of ammonium hydroxide and water) (Figure 11c,d); this method delivered discharge/charge capacities of 1678 and 1249 mA h g⁻¹, which were higher than those of bare Fe₂O₃ (1108 and 806 mA h g⁻¹). In addition, 456 mA h g⁻¹ at 400 mA g⁻¹ and 272 mA h g⁻¹ at 800 mA g⁻¹ were achieved for Fe₂O₃/Co₃O₄ materials as well (Figure 11j–m).

In addition to the abovementioned methods, a template method has been used to prepare other Fe₂O₃/metal-based materials. The 3D ordered macroporous TiO₂/CoPt(α-Fe₂O₃ materials were fabricated by Tang et al. using a sol–gel method, which was templated by poly (methyl methacrylate) microspheres (Figure 11a). The initial discharge/charge capacities of 1563 and 650 mA h g⁻¹ were achieved for the as-synthesized materials at 50 mA g⁻¹. Zeng et al. prepared an α-Fe₂O₃/SnO₂ nanotube array 200–400 nm in diameter (Figure 11g,h) using a template method with a ZnO nanowire array template (Figure 11i), and the synthesized array displayed an excellent discharge capacity of 0.727 mA h cm⁻² over 50 cycles at 0.1 mA cm⁻² during the 1st cycle. In addition, Wang et al. and Zhou et al. also synthesized α-Fe₂O₃/SnO₂ materials. However, Zhou et al. synthesized α-Fe₂O₃/SnO₂ materials by growing SnO₂ nanorods 150 and 20 nm in length and diameter on Fe₂O₃ nanoflakes 10 nm in thickness to achieve a tree-like branched structure. As a result, an areal capacity of 0.43 mA h cm⁻² was obtained by the as-prepared materials after 150 cycles, which was higher than that of pure Fe₂O₃ nanoflakes (0.25 mA h cm⁻²). Hence, Fe₂O₃/SnO₂ materials have been demonstrated as a promising anode material for LIBs. α-Fe₂O₃/SnO₂/carbon materials can be fabricated through a hydrothermal process or in situ polymerization. Du et al. fabricated porous γ-Fe₂O₃/SnO₂/carbon NRs through a hydrothermal method, the precursors of which were FeOOH NRs with 20–40 nm in diameter and 200 nm in length and SnO₂ with 5–10 nm in thickness. It was demonstrated that initial discharge/charge capacities of 1211.1 and 893.7 mA h g⁻¹ were achieved for the as-prepared materials at 200 mA g⁻¹, and the coulombic efficiency was ≈73% during the 1st cycle. Furthermore, the γ-Fe₂O₃/SnO₂/carbon NRs delivered a reversible capacity of 879 mA h g⁻¹ over 60 cycles and a capacitance retention of ≈88%, demonstrating better electrochemical performance compared with SnO₂ and Fe₂O₃/SnO₂. Additionally, in situ polymerization was applied for the synthesis of SnO₂/Fe₂O₃/carbon materials by Guo et al. As a result, the as-synthesized materials delivered the first discharge/charge capacities of 2506 and 1606 mA h g⁻¹ at 200 mA g⁻¹, which were higher than those of the Fe₂O₃/SnO₂ NPs (1175 and 621 mA h g⁻¹). Moreover, the Fe₂O₃/SnO₂/carbon materials exhibited an initial coulombic efficiency of 64%, while that of Fe₂O₃/SnO₂ NPs was only 53% due to the carbon layer.

Fe₂O₃/SnO₂/graphene materials can be prepared by filtration–thermal reduction method and physical blending method. Liu et al. decorated Fe₂O₃/SnO₂ NPs on graphene films with a precursor 40–70 nm in diameter and 200–400 nm in length and SnO₂ NPs of 5 nm in size via filtration–thermal reduction. The as-prepared materials delivered initial discharge/charge capacities of 2063 and 1255 mA h g⁻¹ at 100 mA g⁻¹, which were the highest among those of Fe₂O₃ (1007 mA h g⁻¹), SnO₂ (782 mA h g⁻¹), and graphene (372 mA h g⁻¹), and maintained a reversible discharge capacity of 1015 mA h g⁻¹ over 200 cycles. Lin and Wang prepared Fe₂O₃/SnO₂/GNS films using a physical blending approach, and the films exhibited an initial discharge capacity of 946 mA h g⁻¹ at 100 mA g⁻¹ and retained a value of 538 mA h g⁻¹ over 90 cycles. In addition, Fe₂O₃/SnO₂/rGO materials were fabricated by Xia et al. via a precipitation approach with Fe₂O₃ NPs with ≈20 nm in size, which exhibited the first discharge/charge capacities of 1179 and 746 mA h g⁻¹ at 400 mA g⁻¹. Besides, the as-synthesized materials exhibited a discharge capacity of ≈700 mA h g⁻¹ after 100 cycling tests.

3.3. SIBs

Pure Fe₂O₃, Fe₂O₃/graphene Fe₂O₃/rGO materials have also been synthesized by different methods for good performance in SIBs. γ-Fe₂O₃ films were fabricated by Sun et al. via radio frequency magnetron sputtering by decorating γ-Fe₂O₃ films on Cu sheet substrates. It was demonstrated that the initial discharge/charge capacities of 570 and 510 mA h g⁻¹ were achieved at 500 mA g⁻¹ for the γ-Fe₂O₃ films annealed at 600 °C, which maintained nearly 100% of the initial reversible capacity over 100 charge/discharge cycles. Apart from that, Li et al. prepared the Fe₂O₃/GNSs via a chemical reaction–oxidation method by growing Fe₂O₃ NPs (5 nm in diameter) on graphene nanosheets. As a result, the as-prepared materials exhibited the first discharge/reversible capacities of 542 and 440 mA h g⁻¹ by Fe₂O₃/GNS at 100 mA g⁻¹ and showed 81.2% of the first coulombic efficiency at 250 mA h g⁻¹. Furthermore, a specific capacity of 440 mA h g⁻¹ was achieved at 100 mA g⁻¹, which was higher than that of crystalline Fe₂O₃ with a specific capacity of 284 mA h g⁻¹. Furthermore, the as-synthesized materials delivered a specific capacity of 219 mA h g⁻¹ even at 2 A g⁻¹. Fe₂O₃ nanocrystals with a particle size of ≈2 nm were decorated on GNSs by Jian et al. using a nanocasting approach. It was demonstrated that a capacity of ≈400 mA h g⁻¹ was achieved and maintained by Fe₂O₃/GNS at 100 mA g⁻¹ after 200 cycling tests and the materials delivered a capacity of 190 mA h g⁻¹ at 1000 mA g⁻¹, which was ≈45% of that at 100 mA g⁻¹.

The microwave methodology has also been applied in the synthesis of Fe₂O₃/rGO materials. Zhang et al. fabricated α-Fe₂O₃/rGO materials with α-Fe₂O₃ NPs (50 nm in diameter) and GNSs via a microwave hydrothermal method to deliver a discharge capacity of ≈310 mA h g⁻¹ over 150 cycles at 100 mA g⁻¹. In addition, a microwave-assisted reduction method was applied by Liu and co-workers to prepare Fe₂O₃/rGO materials. It was demonstrated that the Fe₂O₃/30 wt% RGO materials exhibited a reversible capacity of 389.3 mA h g⁻¹, which was higher than that of bare Fe₂O₃/30 wt% RGO of 287.3 mA h g⁻¹ (59% of the initial coulombic efficiency). As a result, a superior reversible capacity of 289 mA h g⁻¹ was obtained by the Fe₂O₃ with 30 wt% RGO at 50 mA g⁻¹ over 5 cycles. In summary, the pure Fe₂O₃ and Fe₂O₃/GNS materials were also superb anode materials for applications as energy storage materials in SIBs.
3.4. Others

Fe₂O₃/nonmetal-based materials, which include B (Boron)-
containing Fe₂O₃ nanocomposites[114] and Fe₂O₃/Se composite
nanorods,[115] have been explored.

Generally speaking, ball milling–heating[114] and oxidation
methods[115] are used for the fabrication of the two different
types of materials. Cao et al. synthesized B-containing Fe₂O₃ materials
using the ball milling–heating method with the Fe₂O₃-
LiBH₄ composites (Figure 12a,b).[114] As shown in Figure 12d–f, pure
Fe₂O₃ exhibited smooth surfaces, while the as-prepared mate-
rials, which were designed as B-containing nanocomposites for
x = 0.1, 0.2, 0.3, and 0.4 (with coulombic efficiencies of 74.6%,
75.9%, 77.2%, and 78.1%, respectively), had NPs with a size
of ≈10 nm decorated on their surfaces. The discharge/charge
potential profiles of the B-containing nanocomposites for x = 0.2
remained constant from 10 to 500 cycles, and the materials dis-
played a specific capacity of 660 mA h g⁻¹ at 2 C, which was
higher than that of pure Fe₂O₃ with 210 mA h g⁻¹ (Figure 12j,k).
In addition, the Fe₂O₃-0.2NaBH₄ materials maintained a capacity
of 1165 mA h g⁻¹ over 200 cycles at 100 mA g⁻¹ (Figure 12l).
Furthermore, Cho et al. obtained Fe₂O₃/Se nanorods via an oxi-
dation method.[115] The as-prepared materials showed different
crystallite sizes of 16, 28, and 39 nm when post-treated at 400,
500, and 600 °C, and the samples were designated as Sel.400-
Oxi.400, Sel.400-Oxi.500, and Sel.400-Oxi.600, respectively
(Figure 12g–i). In addition, it was demonstrated that Sel.400-
Oxi.400 showed the best electrochemical performance among
the three samples and delivered an initial discharge capacity of
1458 mA h g⁻¹, which was higher than the others of 1303 and
1193 mA h g⁻¹ at 1 A g⁻¹. In conclusion, the as-prepared mate-
rials are good candidates for LIBs.

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Figure 12. a) Morphology B-containing Fe₂O₃ nanocomposites. b) Schematic of the preparation process of B-containing Fe₂O₃ nanocomposites.
c) Formation mechanism of the 1D nanostructure comprising porous Fe₂O₃/Se composite and subsequent hollow Fe₂O₃ NRs by nanoscale Kirkendall
diffusion. d) SEM image of pristine Fe₂O₃. e) SEM image of B-containing Fe₂O₃ nanocomposite sample (x = 0.2). f) High-resolution TEM image of the
B-containing sample (x = 0.2). g–i) Morphologies of the 1D nanostructures comprising nanorods obtained after selenization at 400 °C and subsequent
oxidation at 400, 500, and 600 °C. j) Charge/discharge curves at different cycles for the B-containing (x = 0.2) sample at 100 mA g⁻¹. k) Specific capacity
of pristine Fe₂O₃ and B-containing (x = 0.2) samples obtained for cycles at different current densities. l) Cycling performance curves of pristine Fe₂O₃
and B-containing samples prepared from Fe₂O₃-xNaBH₄. (a,b,d,e,j–l) Reproduced with permission.[114] Copyright 2017, Wiley; (c,g,i) Reproduced with
permission.[115] Copyright 2017, Royal Society of Chemistry.
Generally, pure $\alpha$-Fe$_2$O$_3$ and Fe$_2$O$_3$/rGO materials can be fabricated by a hydrothermal approach in LSBs. Rao et al. synthesized $\alpha$-Fe$_2$O$_3$ particles with 20–30 nm in size through a microwave-assisted hydrothermal method.\textsuperscript{116} It was demonstrated that initial discharge/charge capacities of 1364 and 1031 mA h g$^{-1}$ were obtained by the pure $\alpha$-Fe$_2$O$_3$, and it exhibited a reversible capacity of 1000 mA h g$^{-1}$ during the 2nd cycle, showing a capacitance retention of 75.5%. Analogously, $\alpha$-Fe$_2$O$_3$ nanorods with a length of 400 nm and a diameter of $\approx$80 nm anchored on rGO nanosheets ($\alpha$-Fe$_2$O$_3$/rGO NRAs) were synthesized by Kong et al. via a hydrothermal method, as well.\textsuperscript{117} As a consequence, the as-prepared materials delivered the first discharge/charge capacities of 832.0 and 402.4 mA h g$^{-1}$ at 200 mA g$^{-1}$, showing a coulombic efficiency of 48.2%. In addition, the $\alpha$-Fe$_2$O$_3$/rGO NRAs showed a specific capacity of about 420 mA h g$^{-1}$ at 0.1 C, with $\approx$92 mA h g$^{-1}$ even at 1.6 C.

Similarly, bare $\alpha$-Fe$_2$O$_3$ microparticles\textsuperscript{118} and Fe$_2$O$_3$/carbon$\textsuperscript{[119]}$ have been studied for Fe-air batteries. Hang et al. fabricated Fe$_2$O$_3$ with rhombohedra structure with $\alpha$-Fe$_2$O$_3$ (1–10 $\mu$m in size) via a modified polyol method, and this material exhibited an initial discharge capacity of $\approx$320 mA h g$^{-1}\textsuperscript{[118]}$. Besides, chemical methods were used by Hang and Thang to synthesize Fe$_2$O$_3$/carbon materials by decorating Fe$_2$O$_3$ NPs on different types of carbon and it was demonstrated that when employed with tubular CNFs, AB, and graphite, the materials exhibited superb electrochemical performance.\textsuperscript{119}

In conclusion, a brief comparison of the synthesis methods and electrochemical performances of the Fe$_2$O$_3$-based materials for rechargeable batteries is shown in Table 2. It is obvious that, after improving the synthesis approaches and preparing different kinds of Fe$_2$O$_3$-based materials, the capacities have increased compared to pure Fe$_2$O$_3$.

Table 2. Fe$_2$O$_3$-based materials as anodes for rechargeable batteries.

| Materials | Methods | CD$^a$ [C or mA g$^{-1}$] | DC/CC$^b$ [mA h g$^{-1}$] | Capacity [mA h g$^{-1}$]/Cycles |
|-----------|---------|--------------------------|-------------------|-----------------------------|
| Fe$_2$O$_3$\textsuperscript{[120]} | Hydrothermal, annealing | 40,–,– | 900,2,35 |
| 3D network structured Fe$_2$O$_3$\textsuperscript{[121]} | Chemical corrosion, thermal oxidation | C/0.2,895,4,680,6 | 926,1,400 |
| Fe$_2$O$_3$, NRs\textsuperscript{[122]} | Solution-phase growth, chemical etching | C/1,1238,904 | 950,100 |
| Fe$_2$O$_3$/carbon\textsuperscript{[46]} | Surfactant carbonization | C/0.2,1,300,– | 68,50 |
| Fe$_2$O$_3$/carbon\textsuperscript{[123]} | Molten salt process, dispersion in toluene | C/2,1858,– | 2112,100 |
| Fe$_2$O$_3$/carbon NPs\textsuperscript{[124]} | Electrospinning | C/0.2,–,– | 820,100 |
| Fe$_2$O$_3$/MWCNTs\textsuperscript{[125]} | Hydrothermal, annealing | 100,1256,700 | 430,100 |
| Fe$_2$O$_3$/NRs@CNF\textsuperscript{[126]} | Hydrothermal, annealing | 201,1278,896 | 758,50 |
| Fe$_2$O$_3$ particles@graphene\textsuperscript{[127]} | Hydrothermal, annealing | 50,1561,1206 | 1069,50 |
| Fe$_2$O$_3$ particles@rGO\textsuperscript{[128]} | Hydrothermal, annealing | 100,1578,1095 | 950,70 |
| Fe$_2$O$_3$ NPs@rGO\textsuperscript{[129]} | Microwave heating | 1000,979,– | 650,50 |
| Fe$_2$O$_3$/carbon@graphene microspheres\textsuperscript{[130]} | Drying, carbonization, oxidation | 400,1363,– | 841,100 |
| Fe$_2$O$_3$/Fe NPs@graphene\textsuperscript{[131]} | Hydrothermal, in situ thermal reduction | 100,1109,8,2147.5 | 959,3,90 |
| Fe$_2$O$_3$/Co$_3$O$_4$/graphene nanowires\textsuperscript{[132]} | Hydrothermal, hydrolysis | 200,1586,9,– | 1005,1,50 |
| Fe$_2$O$_3$/SnO$_2$/porous nanocubes\textsuperscript{[133]} | Solvothermal, annealing | 200,–,– | 567,5,50 |
| Fe$_2$O$_3$/SnO$_2$/carbon\textsuperscript{[134]} | In situ polymerization in sol, carbonization | 400,2506,1606 | 1000,380 |
| Fe$_2$O$_3$/SnO$_2$/graphene films\textsuperscript{[135]} | Mixing, filtering, freeze-drying, annealing | 100,946,– | 538,90 |
| Fe$_2$O$_3$/NPs@SnO$_2$@rGO\textsuperscript{[136]} | Precipitation, reduction | 400,1179,746 | 700,100 |
| Fe$_2$O$_3$/NRs@N-doped graphene\textsuperscript{[137]} | Hydrothermal, annealing | 2000,–,– | 508,200 |
| Fe$_2$O$_3$ films\textsuperscript{[138]} | Cu template, magnetron sputtering | 500,650,425 | 450,100 |
| Fe$_2$O$_3$ nanocrystals@graphene nanosheets\textsuperscript{[139]} | Nanocasting technique | 100,1103,335 | 400,200 |
| Fe$_2$O$_3$@graphene nanosheets\textsuperscript{[20]} | Chemical reaction–oxidation | 542,100,– | 110,500 |
| $\alpha$-Fe$_2$O$_3$/rGO\textsuperscript{[122]} | Hydrothermal, annealing | –,–,– | 310,150 |
| Fe$_2$O$_3$/rGO\textsuperscript{[113]} | Microwave-assisted reduction | –,–,– | 289,50 |
| SIBs | Fe$_2$O$_3$\textsuperscript{[24]} | Hydrothermal, annealing | C/0.1,1364,1031 | 799,30 |
| Fe$_2$O$_3$\textsuperscript{[134]} | Pyrolysis | –,–,– | –,– |
| $\alpha$-Fe$_2$O$_3$ nanorod@rGO\textsuperscript{[117]} | Seed-assisted hydrothermal, annealing | 200,1837.6,1238.2 | 1200,500 |

$^a$CD: Current density (C or mA g$^{-1}$); $^b$DC/CC: Initial discharge/charge capacity (mA h g$^{-1}$).
4. **Fe$_3$O$_4$-Based Nanomaterials**

4.1. **Supercapacitors**

Fe$_3$O$_4$-based materials, which include pure Fe$_3$O$_4$, Fe$_3$O$_4$/carbon materials, and Fe$_3$O$_4$/metal-based materials (metal or metal oxide)/carbon materials, have been explored in SCs.$^{[32,135,136]}$

4.1.1. **Pure Fe$_3$O$_4$**

Pure Fe$_3$O$_4$ NPs and Fe$_3$O$_4$ thin films can be synthesized through different strategies, which include hydrolysis and the hydrothermal method.$^{[137,138]}$ Wang et al. prepared Fe$_3$O$_4$ NPs with 5–10 nm in diameter by using FeCl$_3$ and the organic solvent ethanolamine.$^{[137]}$ It was demonstrated that a superb capacitance of 207.7 F g$^{-1}$ at 0.4 A g$^{-1}$, a good rate performance (90.4 F g$^{-1}$ at 10 A g$^{-1}$), and a capacity retention of 100% over 2000 cycling tests were obtained for Fe$_3$O$_4$ NPs. Similarly, a hydrothermal method was also adopted by Chen et al. for the synthesis of the Fe$_3$O$_4$ films with particle size of 300 nm–1 µm.$^{[138]}$ As a result, the Fe$_3$O$_4$ films delivered a superb capacitance of 118.2 F g$^{-1}$ at 6 mA g$^{-1}$ and showed a capacitance retention of 88.75% over 500 cycling tests.

4.1.2. **Fe$_3$O$_4$/Carbon Nanomaterials**

Generally, strategies for synthesizing Fe$_3$O$_4$/carbon materials mainly include the reduction method,$^{[139]}$ chemical coprecipitation method,$^{[140]}$ solvothermal/hydrothermal–calcination/sintering method,$^{[141,142]}$ electrospinning technique,$^{[143]}$ solvent-thermal method, and the microwave method.$^{[144]}$

The Fe$_3$O$_4$/carbon core–shell microspheres,$^{[145]}$ Fe$_3$O$_4$-doped double-shelled hollow carbon spheres,$^{[146]}$ and Fe$_3$O$_4$ NPs/carbon$^{[144]}$ have been explored. Liu et al. fabricated Fe$_3$O$_4$/carbon nanosheets (NNSs) with a pore size of >100 nm and a specific surface area of 229 m$^2$ g$^{-1}$.$^{[147]}$ The as-synthesized materials displayed a superb capacitance of 163.4 F g$^{-1}$ at 1 A g$^{-1}$, maintained 113 F g$^{-1}$ even at 10 A g$^{-1}$ and demonstrated a retention of 69.2% (Figure 13i,k). In addition, Wang and...
co-workers synthesized Fe3O4-doped porous carbon nanorods/3D kenaf stem-derived macroporous carbon (Fe3O4-DCN/3D-KSPC) (Figure 13d,e) via a pyrolysis-annealing method (Figure 13a). As a result, the as-prepared materials displayed a high capacitance of 1153 F g⁻¹ at 2 A g⁻¹ and a good rate capability of 514 F g⁻¹ at 100 A g⁻¹. Oh et al. synthesized the oxidized activated carbon/Fe3O4 (AC/Fe3O4) through a reduction method, depositing Fe3O4 NPs with a diameter of 30 nm in poly(vinylpyrrolidone) on AC (Figure 13j). A specific capacitance of 202.6 F g⁻¹ was achieved by the AC/Fe3O4 materials, which was higher than pure Fe3O4 (99.4 F g⁻¹) at 10 mV s⁻¹, and it maintained 94% of the initial value even over 5000 cycles. An electrospinning technique and a solventothermal method were used by Mu and co-workers for the synthesis of Fe3O4 nanosheets on CNFs with 400–500 nm in diameter (Figure 13g). As a result, the as-fabricated Fe3O4/CNFs delivered a specific capacitance of 135 F g⁻¹ while that of bare Fe3O4 was only 83 F g⁻¹, and the materials showed a capacitance retention of 91% over 1000 cycles. In addition, Yun et al. prepared the γ-Fe3O4 nanobox hybrids (γ-Fe NBhs) via a phase controlled solution method and the γ-Fe3O4 is reduced from the α-Fe3O4. It was demonstrated that the specific capacities of the γ-Fe NBhs decreased from 497.7 to 210.3 mAh g⁻¹ while those of hierarchically structured rGO/α-Fe3O4 (rGO/α-Fe) diminished from 662.6 at 50 mA g⁻¹ to 83.6 mAh g⁻¹ at 1000 mA g⁻¹. By contrast, the capacity retention of γ-Fe NBhs was 42.3%, which was higher than that of rGO/α-Fe (12.6%) over 60 cycles at 100 mA g⁻¹. It is the phase transition that contributes to the differences between the two as-prepared materials on the morphology, structure, and electrochemical performances. So, the influences of phase transition should be paid more attention to. The graphene/Fe3O4 NPs or NRs have also been explored through hydrothermal method, a vacuum filtration–drying–peeling off method, an ultrasonication method, and a coprecipitation method. Liu et al. prepared Fe3O4/graphene sheets (GSs) by the vacuum filtration–drying–peeling off method, which grew Fe3O4 NPs of 5 nm on GSs. It was demonstrated that the ideal Fe3O4/GSs (64.8%) with a specific surface area of 310 m² g⁻¹ delivered superb capacitances of 368 F g⁻¹ at 1 A g⁻¹ and 225 F g⁻¹ at 5 A g⁻¹. Lu et al. fabricated Fe3O4/rGO materials with Fe3O4 NPs (20 nm in diameter) through a coprecipitation method, the specific surface area of which was 147 m² g⁻¹. Not only a superb energy density of 43.2 Wh kg⁻¹ at 272.8 W kg⁻¹ but also a good power density of 2183.5 W kg⁻¹ at 27.9 W h kg⁻¹ were observed. Das et al. synthesized Fe3O4 NRs 150 nm in size decorated on rGO materials (186 m² g⁻¹ in specific surface area) with rod structures using an ultrasonication method, which displayed a specific capacity of 315 C g⁻¹ at 5 A g⁻¹ and exhibited an outstanding cyclability retention of 95% over 2000 cycles. Fe3O4 NPs with 5 nm in diameter were anchored on rGO by Li et al. via a hydrothermal method and displayed an excellent capacitance of 241 F g⁻¹ at 1 A g⁻¹. In addition, a cyclability of 79.2% was also observed over 1000 cycling tests at 10 A g⁻¹. Hence, the Fe3O4/graphene materials demonstrate a promising future in applications for SCs.

4.1.3. Fe3O4/Carbon/Metal-Based Nanomaterials

Fe3O4/metal-based materials/carbon including Fe3O4/Fe/CNTs and Fe3O4/MnO2/carbon materials have been synthesized via a chemical synthesis method and electrodeposition method for SCs, respectively. Fe3O4/Fe/CNTs with 20–30 nm outer diameters were prepared by Sun et al. via a chemical synthesis method, and they displayed specific capacitances of 85.29, 70.58, 58.8, 50, and 40.2 F g⁻¹ at 0.5, 1, 2, 5, and 10 A g⁻¹, respectively. In addition, excellent capacitances of 1065 F g⁻¹ at 1 A g⁻¹ and 595.2 F g⁻¹ at 5 A g⁻¹ and a retention of 82.1% at 1 A g⁻¹ over 1000 cycles were achieved by the as-prepared materials, and the retention is higher than that of Fe3O4 nanosheets of 62.3%. Apart from the Fe3O4/Fe/CNTs materials, Sun et al. designed the SCs, the anode materials of which were Fe3O4/MnO2/carbon materials through an electrodeposition method using a conductive yarn substrate, which showed high flexibility. It was demonstrated that areal and volumetric capacitances of 60 and 7.23 mF cm⁻² at 0.9 mA at the 50th cycle and a capacitance retention of 65% were obtained at 3.6 mA. In addition, a discharge capacity of 127 mF cm⁻² at 1 mA, a specific capacity of 60.74 mF cm⁻² at 8 mA, and a high capacity retention of 48% were also achieved by the electrode. Furthermore, the SCs, which were estimated to be 10 cm, 1.5 cm², and 0.0125 cm³ in length, area, and volume, exhibited energy densities of 0.005 mW h cm⁻³, 0.0335 mW h cm⁻², and 4.02 mW h cm⁻³.

In conclusion, the Fe3O4/metal-based/carbon materials are promising anode materials for practical applications in SCs, especially when the conductive substrate is applied for superb flexibility.

4.2. LIBs

Pure Fe3O4, Fe3O4/graphene materials, and Fe3O4/metal-based materials (metal or metal oxide) were explored in LIBs for electrochemical performance. In addition to Fe2O3, different morphologies of bare Fe3O4, including Fe3O4 NPs, Fe3O4 NWs, Fe3O4 microspheres, Fe3O4 octahedra, Fe3O4 hexahedra, hollow Fe3O4 beads, Fe3O4 thin films, and Fe3O4 nanocubes have been studied. Generally, strategies for preparing pure Fe3O4 mainly include hydrothermal/solvothermal method and the template-electrochemical deposition method. Wang et al. prepared flower-like bare Fe3O4 with Fe3O4 nanoplates of about
60 nm in thickness (Figure 14a,b). A reversible capacity of 1000.3 mA h g\(^{-1}\) was observed over 50 cycles for the pure Fe\(_3\)O\(_4\) microflowers, while the Fe\(_3\)O\(_4\) microspheres only exhibited a reversible capacity of 305.3 mA h g\(^{-1}\) (Figure 14o). Su et al. prepared Fe\(_3\)O\(_4\) NWs 50 nm in diameter (Figure 14c,d) via a hydrothermal method, and they displayed an initial discharge capacity of 1868 mA h g\(^{-1}\) even at 500 mA g\(^{-1}\).[161] In addition, the pure Fe\(_3\)O\(_4\) microflowers maintained a discharge capacity of 906 mA h g\(^{-1}\) even at 500 mA g\(^{-1}\). Zhang et al. fabricated Fe\(_3\)O\(_4\) spheres with 400–500 nm diameters (Figure 14e,f) using a solvothermal method, and they displayed initial discharge/charge capacities of 1316 and 933 mA h g\(^{-1}\) at 500 mA g\(^{-1}\) and exhibited a coulombic efficiency of 70.9%.[168] Wu et al. synthesized Fe\(_3\)O\(_4\) electrodes with a template method based on Cu, and they deposited Fe\(_3\)O\(_4\) on the template (Figure 14g). It was demonstrated that a reversible capacity of 1382 mA h g\(^{-1}\) over 100 cycles at 1 A g\(^{-1}\) was obtained for the Fe\(_3\)O\(_4\) electrodes. Furthermore, initial discharge/charge capacities of 1308 mA h g\(^{-1}\) and 983 mA h g\(^{-1}\) were observed for the pure Fe\(_3\)O\(_4\) with a coulombic efficiency of 75% during the 1st cycle.
Besides, a thermal decomposition approach\(^{[171]}\) and coprecipitation method\(^{[188]}\) have been applied to the fabrication of the materials. Lee et al. prepared mesoporous Fe\(_3\)O\(_4\) NP (11–12 nm in size) clusters (MIONCs) by a thermal decomposition approach (Figure 14n), and they displayed a reversible capacity of 867 mA h g\(^{-1}\) during the 1st cycle.\(^{[171]}\) Behera et al. fabricated Fe\(_3\)O\(_4\) NPs through a coprecipitation method, displaying a capacity of 1470 mA h g\(^{-1}\) for the 1st cycle and showing a reversible capacity of 1084 mA h g\(^{-1}\) at 100 mA g\(^{-1}\).\(^{[158]}\)

### 4.2.2. Fe\(_3\)O\(_4\)/Carbon Nanomaterials

Fe\(_3\)O\(_4\)/carbon materials can be synthesized through the hydrothermal/solvothermal–annealing/calcination method.\(^{[172–175]}\) Ding et al. prepared Fe\(_3\)O\(_4\)/carbon microspheres, which consisted of pores with a diameter of 68 nm, carbon layers with a thickness of 21 nm, and Fe\(_3\)O\(_4\) nanocrystals with 8.1 nm in size (Figure 14lm), via a hydrothermal process.\(^{[176]}\) It was demonstrated that the as-prepared materials delivered Fe\(_3\)O\(_4\)/carbon microspheres exhibiting a superb discharge capacity of 1231.3 mA h g\(^{-1}\) at 0.5 A g\(^{-1}\) after 100 cycles. In addition, discharge capacities of 1017.2 and 601.9 mA h g\(^{-1}\) were obtained by the Fe\(_3\)O\(_4\)/carbon microspheres at 1 and 5 A g\(^{-1}\) over 500 cycles, respectively. Fe\(_3\)O\(_4\)/carbon materials with a flower-like structure (2 \(\mu\)m in diameter) (Figure 14h–k) were prepared by Deng and co-workers via a solvothermal–calcination method in \(N_2\).\(^{[177]}\) It was demonstrated that the as-prepared materials delivered a specific capacity of 227 mA h g\(^{-1}\) at 5 C, which was higher than that of hollow microspheres and dispersed nanoflakes with specific capacities of 45 and 10 mA h g\(^{-1}\).

Apart from above, polymerization–heat treatment process\(^{[178–180]}\) can also be used for the preparation of the Fe\(_3\)O\(_4\)/carbon materials. Jung and co-workers fabricated Fe\(_3\)O\(_4\)/carbon microspheres using a polymerization–annealing two-step process.\(^{[180]}\) The as-prepared samples were divided into three different kinds, namely, S1001, S1005, and S1010. Among them, the S1001 had the largest average diameter because the Fe\(_3\)O\(_4\) NPs/CA in this sample was scarce. Furthermore, S1005 was smoother than S1010. A discharge capacity of 1225 mA h g\(^{-1}\) was obtained by S1010 for the 1st cycle (Figure 14p). In addition, Wu et al. synthesized Fe\(_3\)O\(_4\)/carbon materials by mixing Fe(NO\(_3\))\(_3\), citric acid, and NaCl in the solution and drying them to form a citric acid network, which was embedded with Fe nitrate and NaCl.\(^{[181]}\) As a result, the Fe\(_3\)O\(_4\)/carbon materials exhibited a reversible capacity of over 780 mA h g\(^{-1}\) over 20 cycles and 834 mA h g\(^{-1}\) over 60 cycles (Figure 14q). Furthermore, the as-prepared materials displayed discharge/charge capacities of 1415 and 1050 mA h g\(^{-1}\) while the Fe\(_3\)O\(_4\) NPs only exhibited 1262 and 929 mA h g\(^{-1}\) (Figure 14q).

Fe\(_3\)O\(_4\) nanocrystals/GNSs,\(^{[182]}\) Fe\(_3\)O\(_4\)/graphene hollow spheres,\(^{[183]}\) Fe\(_3\)O\(_4\)/graphene hollow nanospheres,\(^{[183]}\) Fe\(_3\)O\(_4\)/graphene films,\(^{[185]}\) Fe\(_3\)O\(_4\)/graphene microsheets decorated on GNSs,\(^{[186]}\) and Fe\(_3\)O\(_4\) NPs wrapped by graphene nanoscrolls\(^{[187]}\) have also been explored. Zhou et al. anchored Fe\(_3\)O\(_4\) NPs on GNSs (Figure 15a,b) using an in situ reduction method, and the size of the Fe\(_3\)O\(_4\) particles decreased to 428 nm over 30 cycling tests.\(^{[188]}\) It was demonstrated that Fe\(_3\)O\(_4\)/GNS materials displayed a charge capacity of 900 mA h g\(^{-1}\), while commercial Fe\(_3\)O\(_4\) particles only exhibited 770 mA h g\(^{-1}\) for the 1st cycle. Furthermore, a specific capacity of 520 mA h g\(^{-1}\) at 1750 mA g\(^{-1}\), which was 53% of the initial capacity, was also obtained for the as-prepared materials. Zhao et al. fabricated Fe\(_3\)O\(_4\)/GNSs using a preparation method (Figure 15g).\(^{[189]}\) The initial discharge/charge capacities of Fe\(_3\)O\(_4\)/GNSs and Fe\(_3\)O\(_4\)/GNSs were 1720 and 1410 mA h g\(^{-1}\), and 1060 and 960 mA h g\(^{-1}\) at 0.1 C, respectively. Luo et al. synthesized the Fe\(_3\)O\(_4\)/graphene materials via an atomic layer deposition method, which delivered an initial capacity of 1192 mA h g\(^{-1}\), which decreased to 785 mA h g\(^{-1}\) for the 2nd cycle at 1 C, leading to a coulombic efficiency of \(\approx 66\%.\(^{[190]}\) In addition, the as-prepared materials exhibited a discharge capacity of 785 mA h g\(^{-1}\) at 1 C and retained that capacity for 500 cycles (Figure 15i,j). Ren et al. prepared Fe\(_3\)O\(_4\)/graphene materials via a hydrothermal method (Figure 15c,d).\(^{[191]}\) As a result, the Fe\(_3\)O\(_4\)/graphene materials displayed a superb reversible capacity of 1164 mA h g\(^{-1}\) after 500 cycling tests at 500 mA g\(^{-1}\).

Fe\(_3\)O\(_4\)/rGO materials can be fabricated by a solvothermal method,\(^{[192]}\) deposition method,\(^{[193]}\) and ultrasonication–heat treatment technology.\(^{[194]}\) Chen and co-workers synthesized Fe\(_3\)O\(_4\)/rGO materials with Fe\(_3\)O\(_4\) particles (160 nm in diameter) using a solvothermal method (Figure 15e,f), and initial discharge/charge capacities of 1912 and 1450 mA h g\(^{-1}\) were achieved by the as-synthesized materials, while those of pure Fe\(_3\)O\(_4\) were only 1342 and 991 mA h g\(^{-1}\) at 92.4 mA g\(^{-1}\).\(^{[192]}\) Furthermore, Fe\(_3\)O\(_4\)/rGO materials maintained a capacity of 1547 mA h g\(^{-1}\), which was higher than that of pure Fe\(_3\)O\(_4\) 775 mA h g\(^{-1}\) during the 5th cycle. In addition, the materials also exhibited a superb reversible capacity of 1031 mA h g\(^{-1}\) over 50 cycles, which was 84% of the initial value. Bhuvaneswari et al. synthesized Fe\(_3\)O\(_4\)/rGO materials by decorating Fe\(_3\)O\(_4\) particles on rGO (Figure 15h), which displayed specific capacities of \(\approx 612\) and \(\approx 446\) mA h g\(^{-1}\) at 1 and 5 C, respectively.\(^{[195]}\) Zhang et al. fabricated Fe\(_3\)O\(_4\) nanocrystal/rGO papers (about 2 nm) via an ultrasonication–heat treatment technology, which exhibited a superb reversible capacity of 1140 mA h g\(^{-1}\) at 1 C.\(^{[194]}\) It was demonstrated that the mechanical mixture of rGO and Fe\(_3\)O\(_4\) (MM-rGO-F) delivered a specific capacity of 150 mA h g\(^{-1}\) while the thermally annealed Fe\(_3\)O\(_4\)/rGO hybrid papers (TA-rGO-F) showed a reversible capacity of \(\approx 1140\) mA h g\(^{-1}\) for 220th cycle and the powdered rGO/Fe\(_3\)O\(_4\) (P-rGO-F) displayed the first reversible capacity of 1521 mA h g\(^{-1}\) (Figure 15k,l).

Generally, Fe\(_3\)O\(_4\)/carbon/graphene materials can be synthesized by a hydrothermal/solvothermal method.\(^{[195–197]}\) Zuo et al. fabricated homogeneously anchored H-Fe\(_3\)O\(_4\) NPs (100–150 nm in diameter) on graphene nanosheets (H-Fe\(_3\)O\(_4\)/carbon/GNSs) via a hydrothermal method, which exhibited an initial discharge capacity of 1331.7 mA h g\(^{-1}\) at 0.1 C, while those of pure Fe\(_3\)O\(_4\) and graphene were only 926 and 744 mA h g\(^{-1}\), respectively.\(^{[196]}\) Similarly, the hydrothermal method was also used by Fan and co-workers for the fabrication of Fe\(_3\)O\(_4\)/carbon/graphene materials by decorating GNSs with Fe\(_3\)O\(_4\)/carbon NPs 50 nm in size.\(^{[197]}\) It was demonstrated that the as-prepared Fe\(_3\)O\(_4\)/carbon/graphene materials displayed initial reversible capacities of 1016.6 and 1199.8 mA h g\(^{-1}\) (Figure 15k,l).

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electrochemical performance with a good reversible capacity of 1468 mA h g\(^{-1}\) and a superb cycle stability of 1200 mA h g\(^{-1}\) over 100 cycling materials at 0.2 A g\(^{-1}\).[195] Zhao et al. prepared Fe\(_3\)O\(_4\)/carbon/graphene materials with a sandwich morphology and found that the as-prepared materials displayed capacities of \(\approx 1481\) mA h g\(^{-1}\) for the 1st cycle and \(\approx 860\) mA h g\(^{-1}\) over 100 cycles at 0.1 C.[198] Hence, the Fe\(_3\)O\(_4\)/carbon/graphene materials are superb anode materials for high performance in LIBs.

4.2.3. Fe\(_2\)O\(_3\)/Metal-Based Nanomaterials

Fe\(_2\)O\(_3\)/metal-based materials, which include Fe\(_2\)O\(_3\)/Cu NWs,[199] Fe\(_2\)O\(_3\)/Ni films,[200] Fe\(_2\)O\(_3\)/γ-Fe\(_2\)O\(_3\) microspheres,[201] Fe\(_2\)O\(_3\)/CuO NWs[202] and Fe\(_2\)O\(_3\) NPs dropped on TiO\(_2\) nanofibers[203] have also been tested as anodes for LIBs; they delivered a good capacity of 390 mA h g\(^{-1}\) over 50 cycles at 200 mA g\(^{-1}\) (Figure 16i).[204] Similarly, a hydrothermal–heat treatment method was also used by Li et al. for the fabrication of Fe\(_2\)O\(_3\)/Ni/carbon nanoplate arrays (Figure 16g).[205] The as-prepared materials showed discharge capacities of 832.5 and 279 mA h g\(^{-1}\) at 0.3 and 4.5 C over 50 cycles, respectively. In addition, the materials maintained a specific capacity of 279 mA h g\(^{-1}\) at 4.5 C. Furthermore, Wang et al. decorated Fe\(_2\)O\(_3\)/NPs on TiO\(_2\) nanofiber (\(\approx 220\) nm in diameter) hierarchical heterostructures (FTHs) by combining the electrospinning and hydrothermal methods together (Figure 16e,f).[203] The initial discharge/charge capacities of 783.6 and 494.5 mA h g\(^{-1}\) were achieved for the as-synthesized materials at 100 mA h g\(^{-1}\) at 4.5 C. In addition, the materials even showed a reversible capacity of 454.5 mA h g\(^{-1}\) over 200 cycles (Figure 16k,l).

Apart from the hydrothermal method, the electrochemical plating method[200] and sol–gel polymerization–heat-treatment method[206] have also been used for the synthesis of Ni/Fe\(_2\)O\(_3\)
films and Fe₃O₄/Fe/carbon materials. Xiong et al. prepared porous Fe₃O₄/Ni films (the Ni film was 200–300 nm in diameter) with flower structures via an electrochemical plating method (Figure 16a,b). The initial discharge/charge capacities of 1324.3 and 1138.6 mA h g⁻¹ at 0.1 C were achieved for the as-synthesized materials, and they were higher compared with the value for the pure Fe₃O₄ film (873.7 and 582.6 mA h g⁻¹). In addition, the initial coulombic efficiency of the Fe₃O₄/Ni films was 86.0%, whereas that of the Fe₃O₄ films was 66.7%. Hence, the materials displayed an outstanding cycle stability (951.9 mA h g⁻¹ at 1 C over 50 cycles) and a superior rate capability (729.5 mA h g⁻¹ at 5 C). The sol-gel polymerization and heat-treatment methods were used by Zhao and co-workers for the fabrication of Fe₃O₄/Fe/carbon materials (Figure 16j). The Fe₃O₄/Fe/carbon electrodes exhibited initial discharge/charge capacities of 1192 and 685 mA h g⁻¹ at 50 mA g⁻¹, while the specific capacities of the Fe₃O₄ and carbon were only 926 and 372 mA h g⁻¹. Zhang et al. prepared mesoporous biocarbon fibers (Fe₃O₄/Fe/MBCFs) by using a natural cotton biotemplate (Figure 16c,d). The Fe₃O₄/Fe/MBCFs exhibited an initial reversible capacity of 1340.5 mA h g⁻¹ at 1 A g⁻¹, a reversible capacity of 533.2 mA h g⁻¹ in the 10th cycle and maintained 524.6 mA h g⁻¹ after 60 cycling tests. In summary, Fe₃O₄-MOX are superb candidates for high electrochemical performance in energy storage devices.

A Fe₃O₄ nanoflake/N-doped carbon matrix (Fe₃O₄ NFs/NC) N-doped carbon wrapped Fe₃O₄ (N-mFe₃O₄/Carbon) nanospheres N-doped Fe₃O₄/carbon materials with an urchin structure and Fe₃O₄/NC have been explored.

N-doped Fe₃O₄/carbon materials are mainly synthesized via hydrothermal/solvothermal–annealing method. The
N-doped FeO\textsubscript{4}/carbon materials with an urchin morphology (500 nm–1 \textmu m) were prepared by Chen and co-workers via a hydrothermal–carbonization method, and as a result, a reversible capacity of 800 mA h g\textsuperscript{−1} over 100 cycles at 500 mA g\textsuperscript{−1} was obtained for the materials.\cite{211} Guo et al. fabricated FeO\textsubscript{4} NF/NC with FeO\textsubscript{4} NF (50–60 nm in width) and NC (10 nm in thickness).\cite{219} The as-prepared materials (proportion of carbon is 44%) displayed reversible capacities of 1046 mA h g\textsuperscript{−1} at 0.2 C after 200 cycles, 662 mA h g\textsuperscript{−1} at 1 C over 500 cycles, and 600 mA h g\textsuperscript{−1} at 5 C after 200 cycles, showing superior performance in LSBs. Similarly, Meng et al. prepared N-mFeO\textsubscript{4}/carbon materials with FeO\textsubscript{4} particles (=115 nm in size) and a carbon coating (2–5 nm in thickness), and they displayed a reversible capacity of 1273 mA h g\textsuperscript{−1} after 200 cycles at 0.2 C and showed an outstanding rate capability of 596 mA h g\textsuperscript{−1} at 1 C and 441 mA h g\textsuperscript{−1} at 2 C.\cite{210} Wang et al. fabricated FeO\textsubscript{4}/CN core–shell microspheres with a peanut structure using a solvothermal method, and they displayed a reversible capacity of 670 mA h g\textsuperscript{−1} at 0.01–3.0 V over 30 cycles and were higher than that of pure FeO\textsubscript{4} (100 mA h g\textsuperscript{−1}).\cite{212} Hence, the N-doped FeO\textsubscript{4}/carbon materials are proved to be superb candidates in LSBs.

4.3. SIBs

FeO\textsubscript{4} NPs,\cite{211} octahedral FeO\textsubscript{4}/carbon materials,\cite{214} and FeO\textsubscript{4} quantum dots implanted in microcarbon/graphene (N source) materials (FeO\textsubscript{4} QD/C-GN)\cite{215} have been explored in SIBs for superb electrochemical performance. Pure FeO\textsubscript{4} NPs (<10 nm) were fabricated by Kumar and co-workers via a hydrothermal method, and they exhibited an initial discharge capacity of 590 mA h g\textsuperscript{−1} and a reversible capacity of 248 mA h g\textsuperscript{−1} over 50 cycles at 0.1 C.\cite{213} In addition, Li et al. synthesized the FeO\textsubscript{4}/carbon nano-octahedra with 300–500 nm diameters through a pyrolysis method. It was demonstrated that initial discharge/charge capacities of 824.5 and 496.2 mA h g\textsuperscript{−1} were achieved by the as-obtained materials at 100 and 500 mA g\textsuperscript{−1}, respectively.\cite{214} In addition, the FeO\textsubscript{4}/carbon materials also exhibited coulombic efficiencies of 60.2% and 53.9% for the 1st cycle at 100 and 500 mA g\textsuperscript{−1}, respectively. Qi et al. obtained the FeO\textsubscript{4} QD/C-GN materials on a substrate of metal organic frameworks using an in situ quantization method.\cite{215} The as-prepared materials showed initial discharge/charge capacities of 1081 and 971 mA h g\textsuperscript{−1} and a coulombic efficiency of 62.4% at 200 mA g\textsuperscript{−1}, which were higher compared to the values for bulk FeO\textsubscript{4}–C (680, 461 mA h g\textsuperscript{−1}, 44.5%). In summary, pure FeO\textsubscript{4}, FeO\textsubscript{4}/carbon materials and FeO\textsubscript{4} QD/C-GN materials all exhibit great potential for applications in energy storage devices.

4.4. Others

FeO\textsubscript{4} or FeO\textsubscript{4}-based materials are also applied in other batteries including LSBs, alkaline secondary batteries, and Fe/air batteries. FeO\textsubscript{4} NP/graphene materials with a particle size of 40–60 nm for LSBs were obtained by Fu et al. through a coprecipitation method.\cite{216} As a result, a specific capacity of 1430 mA h g\textsuperscript{−1} over 100 cycling tests at 200 mA g\textsuperscript{−1} was reached by the as-fabricated materials. Furthermore, the FeO\textsubscript{4} NPs/graphene materials exhibited discharge capacities of 855 and 210 mA h g\textsuperscript{−1} for the 1st cycle and over 40 cycles, respectively. Similarly, a coprecipitation method was also used by Li et al. for the synthesis of pure FeO\textsubscript{4} in alkaline secondary batteries.\cite{217} The as-prepared materials annealed at 700 °C performed best, delivering discharge capacities of 587.6, 539.5, and 500.1 mA h g\textsuperscript{−1} at 240, 600, and 1200 mA g\textsuperscript{−1}, respectively. In addition, Ito et al. fabricated FeO\textsubscript{4}/tubular carbon nanofibers (the CNFs were 50 nm in diameter) (FeO\textsubscript{4}/TCNFs) for Fe/air batteries, and they displayed a good capacity of 786 mA h g\textsuperscript{−1} and a cycling efficiency of 76% after 30 cycles.\cite{217}

A brief comparison of the synthesis methods and electrochemical performances of the FeO\textsubscript{4}-based materials for rechargeable batteries is shown in Table 3.

5. FeO-Based Nanomaterials

FeO is black powder without magnetism which can be applied in electrochemical energy storage, including SCs\cite{226} and LIBs,\cite{227–229} A method which using oleic acid (OA) and oleylamine (OAm) to react with iron(III) acetylacetonate ([Fe(acac)\textsubscript{3}]) at high temperature to synthesize the FeO NPs was reported by Hou et al.\cite{220} In fact, pure FeO NPs are difficult to prepare because they were easy to be oxidized to Fe\textsubscript{3}O\textsubscript{4} and Fe\textsubscript{3}O\textsubscript{4} owing to the chemically unstable structure. Hydrothermal method was used for the synthesis of FeO/CVO with FeO nanospheres and CVO (cobalt vanadium oxide hydrate) in SCs by Centre et al.\cite{226} It was demonstrated that a specific capacitance of 968 mA h g\textsuperscript{−1} was achieved at 1 A g\textsuperscript{−1} and a capacitance retention of 95% was achieved after 5000 cycles.

FeO/C,\cite{227} FeO\textsubscript{4}/FeO/Fe,\cite{228} FeO\textsubscript{4}/FeO/Fe/C\cite{229} have been investigated as anode materials for LIBs, respectively. Carbothermally reduction method, solid method, and hydrothermal-treatment method can be used to synthesize them. Gao et al. synthesized the FeO/C anode materials from nano FeO\textsubscript{4} combined with acetylene black (AB) via a carbotherm reduction method.\cite{227} It was demonstrated that the initial discharge/charge capacities of FeO/C composites with carbon ratio of 30, 40, 50, 60, 70 wt% are 653, 760, 719 645, 630 mA h g\textsuperscript{−1} at 1 C, respectively. So, the FeO/C (40 wt%) materials performed better with a coulombic efficiency of 74% at the 1st cycle. Research on the FeO\textsubscript{4}/FeO/Fe was done by Shi et al. and they found that an initial discharge capacity and a coulombic efficiency of 286.5 mA h g\textsuperscript{−1} and 90.8% was achieved at 5 C.\cite{228} Zhao et al. prepared the FeO\textsubscript{4}/FeO/Fe/C materials by a hydrothermal-treatment method without any templates.\cite{229} The discharge capacities of 1722 and 550 mA h g\textsuperscript{−1} were achieved in the 1st and 60th at 88 mA g\textsuperscript{−1}, respectively.

In general, synthesis for composites which combine FeO with Fe\textsubscript{3}O\textsubscript{3} or Fe\textsubscript{3}O\textsubscript{4} is easy while that of pure FeO is complex and difficult. The controlled oxidation of the FeO NPs will result in the formation of Fe\textsubscript{2}O\textsubscript{3} or Fe\textsubscript{3}O\textsubscript{4} NPs. So, when the reversible capacity and rate capability are tested at different temperatures, the component of the composites may change.
That is why there are very few applications of FeO in electrochemical energy storage.

6. Conclusions and Outlook

Currently, FeO have been paid more attention because of the good theoretical capacity, rich abundance, low cost, and environmental friendliness. Apart from the advantages, they also have the drawbacks of poor conductivity and unstable structures. To overcome the problems, considerable efforts have been done by the scientists for better electrochemical performances. This review provides an overview of FeO (Fe2O3/Fe3O4)-based materials for applications in energy storage devices, including SCs, LIBs, SIBs, and other batteries.[231,232] The synthetic methods, morphologies, and electrochemical performance are mainly introduced. The combination of different materials with Fe2O3/Fe3O4 achieved electrochemical properties of high capacity, good rate capability, and cycling life.

It is crucial to improve the undesirable electrochemical and cycling performance of FeO caused by the poor conductivity and unstable structures. Three kinds of materials, including carbon-based materials (amorphous carbon, graphene, CNTs, and so on), conductive polymers (polymer polypyrrole (PPy), polyaniline (PANI), polythiophenes (PTh), and poly(3,4-ethylenedioxythiophene (PEDOT)), and metal materials (metal NPs and metal substrates such as Ni/Cu foam) have been used combined with FeO for enhanced conductivity. Besides, desirable structures are designed for large surface areas and good mechanical and chemical abilities, including nanowires, nanorods, nanosheets, nanotubes, and so on, to accelerate the transfer of the charge and shorten the ion diffusion pathway.

Apart from the advanced achievements, challenges and bottleneck still exist: 1) The crystal structures may have some effects on electrochemical performance so investigation of this aspect should be focused. 2) The interaction force between the combination of FeO and other different materials may interfere with the charge transfer and more research should be done to investigate the mechanism in this respect and avoid the disadvantages. 3) The synthesis for pure FeO is difficult and the components of FeO-based materials are changeable so that the research on the electrochemical performances is lacking, which causes the shortage of applications for electrochemical energy storage. To achieve more desired performance characteristics, future directions in the study of applications for FeO-based materials for energy storage are as follows: 1) Unique nanostructures and porous structures with large surface areas are required for improving the transport and activities of the electrodes. 2) Highly conductive substrates should be utilized for the synthesis of integrated electrodes. The FeO materials grown on the substrates with nanowire, nanotube, and nanorod morphologies possess good conductivity and superb cycle stability. 3) Flexible energy storage devices based on FeO-based materials should be more widely studied for practical applications.[233] 4) Considerable efforts should be made in

\[\text{Table 3. Fe}_3\text{O}_4\text{-based materials as anodes for rechargeable batteries.}\]

| Materials       | Methods                        | CD\(^a\) [C or mA g\(^{-1}\)] | DC/CC\(^b\) [mA h g\(^{-1}\)] | Capacity [mA h g\(^{-1}\)]/Cycles |
|-----------------|--------------------------------|-------------------------------|---------------------------------|-----------------------------------|
| LiBs            |                                |                               |                                 |                                   |
| Fe3O4 nanowires  | Hydrothermal, annealing         | 500,1868,–                     |                                 | 503,100                           |
| Fe3O4            | Solvothermal method            | 100,1365.4,1084.1              | 1000,3,50                       |
| Fe3O4 NPs@C     | Sulfur-calination, annealing    | 924,–,–                        | 773,200                         |
| Fe3O4 particles  | Self-assembly, syn-carbonization| 100,–,–                        | 932,100                         |
| Fe3O4 nanocrystals@CNT | Coprecipitation, sonication, oil bath | C/0.1,–,–                      | 850,100                         |
| Fe3O4@C composite nanofibers | Electrophoresis, carbonization | 200,1551,–                     | 1000,80                          |
| Fe3O4@C films   | Solvothermal method, annealing  | 100,–,–                        | 1038,100                        |
| Fe3O4 NPs@rGO   | Coprecipitation, reduction      | 1000,–,–                       | 300,100                         |
| Fe3O4@C@C       | Hydrothermal, annealing         | 200,1450.7,1016.6              | 633,5,500                       |
| Fe3O4@Fe@C      | Sol–gel polymerization, heat-treatment | 50,1192,685                   | 600,40                          |
| Fe3O4@FeO2 NRs  | Hydrothermal, calcination       | C/0.1,1230.4,955.8             | 893,3,50                        |
| Fe3O4@FeO2@C NRs| Hydrothermal, annealing         | C/0.05,2008,–                  | 435,50                          |
| Fe3O4@N@C      | Hydrothermal, carbonization     | 500,–,–                        | 800,100                         |
| SIBs            |                                |                               |                                 |                                   |
| Fe3O4 NPs       | Hydrothermal, annealing         | 83,590,–                       | 248,30                          |
| Fe3O4@C nanoctahedra | Pyrolysis                  | 100,643,–                      | 380,60                          |
| Fe3O4@graphene sheets | Hummers method             | 200,1081,971                   | 343,200                         |
| LSBs            |                                |                               |                                 |                                   |
| Fe3O4 NPs@C     | Coprecipitation, annealing      | 200,2670,–                     | 1430,100                        |

\(^a\text{CD: Current density (C or mA g}^{-1}\); \(^b\text{DC/CC: Initial discharge/charge capacity (mA h g}^{-1}\).}
componential regulation, elemental doping, and defect modification for better electrochemical performance. 5) Due to the advantages of surface modification on electrodes, development of new active materials, and design of optimized nanostructures, ALD method should be paid more attention for the improved rate capability and cycling stability. In summary, rapid progress has been achieved for FeO$_x$-based materials resulting in good electrochemical performance, and FeO$_x$-based materials are expected to have broad applications in electrochemical energy storage.

**Acknowledgements**

This work was supported by the National Natural Science Foundation of China (NSFC-21671710, 21673203, and 21201010), the Top-notch Academic Programs Project of Jiangsu Higher Education Institutions (TAPP), Program for New Century Excellent Talents of the University in China (NCET-13-0645) and Innovation Scientists and Technicians Troop Construction Projects of Henan Province (164200510018), Postgraduate Research & Practice Innovation Program of Jiangsu Province (XYXXC17-038), the Six Talent Plan (2015-XCL-030), and Qinglan Project. We also acknowledge the Priority Academic Program Development of Jiangsu Higher Education Institutions and the technical support we received at the Testing Center of Yangzhou University.

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

batteries, electrochemical energy storage, FeO$_x$-based materials, supercapacitors

Received: December 7, 2017
Revised: January 30, 2018
Published online: April 23, 2018

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