Supercapacitors

Nanostructured Iron Oxide/Hydroxide-Based Electrode Materials for Supercapacitors

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Abstract: There is a pressing need to further increase the energy density of supercapacitors to meet the requirements of next-generation electronic devices. One promising solution is to develop advanced electrode materials with large capacitance at fast charge/discharge rates. Among the newly developed electrode materials for supercapacitors, iron oxides/hydroxides have recently emerged as a promising class of anode materials largely because of their attractive electrochemical performance, source abundance, low price, and environmental friendliness. However, the use of these emerging materials in practical set-ups is unfortunately curtailed by their relatively small surface area and poor electrical conductivity, which could pose detrimental effects on their pseudocapacitive performance. Recently, material scientists and chemists in the energy community have attempted to address these materials’ challenges by taking the advantage of the unique physical and chemical properties of iron oxides/hydroxides at the nanoscale size regime, which are the key topics discussed in this Focus Review. Here, we first summarize recent advances in the development of high-performance iron oxide/hydroxide-based electrode materials, and their use as anode materials in asymmetric supercapacitors. We then highlight and exemplify several effective design strategies, such as architectural design, chemical modification, and multifunctional composites of iron oxide/hydroxide-based electrodes, to further improve their electrochemical properties. In the last section, we discuss the challenges and perspectives in this exciting field, shedding some light on the design of iron oxide/hydroxide-based electrodes for practical applications.

1. Introduction

In the era of a fast growing global economy, the ever-increasing consumption of fossil fuels and the associated environmental deterioration have stimulated an urgent and strong demand for green and renewable energy sources, such as solar and wind power.\(^1,2\) These renewable energy sources are intermittent, and require the help of energy storage devices to regulate the power fluctuations for smart grid applications. In addition, the exploding markets for portable electronics and electric vehicles have also attracted tremendous interest in developing various energy storage devices as the power supply.\(^3\) Among the emerging energy storage technologies, lithium-ion batteries and supercapacitors are at the pivotal realm of the research as these technologies have already been widely used in our daily life in powering consumer electronics.\(^6,7\)

Recently, supercapacitors, also known as electrochemical capacitors, have emerged as a promising class of energy storage devices in both industry and academia, largely owing to their high power density, fast charge/discharge rate, long cycle life, and low maintenance cost.\(^7\) In particular, supercapacitors can deliver a higher energy density than the traditional capacitors, and they also feature a higher power density compared with batteries. Therefore, supercapacitors could bridge the power gap between batteries and capacitors, finding increasing acceptance in back-up power systems, power tools, and electric vehicles.\(^9\) Unfortunately, the energy density of the commercialized supercapacitors is still low (\(\sim 10\) Wh kg\(^{-1}\)), and this does not satisfy the ever-increasing energy requirement of next-generation electronic devices. There is, therefore, a pressing need to develop advanced supercapacitors with high energy density and without compromising their high power density and long cycle life. Such challenging issues could be largely addressed by the delicate design of electrode materials with good electrochemical performance.

In general, increase of the output voltage and the specific capacitance can improve the energy density of supercapacitors.\(^7\) An effective way to maximize the output voltage is to choose a pair of anode and cathode materials with a desirable potential difference. Another promising solution is the development of high-capacity electrode materials with optimal electrode architecture. Based on the charge storage mechanism, the electrode materials can be divided into two categories.\(^9\) The first is double-layer capacitive electrode materials that can store the charge at the electrode/electrolyte interface. The second is pseudocapacitive electrode materials, which rely on reversible redox reactions between the electrode materials and the electroactive species in the electrolytes. In general, pseudocapacitive electrode materials can deliver much higher specific capacity than double-layer capacitive electrode materials, and they are considered as a promising class of materials with improved energy density for supercapacitors.

One promising class of pseudocapacitive electrode materials are transitional metal oxides/hydroxides, as the multiple valence states of the metal ions in these materials could enable a fast faradaic redox reaction near to the surface region.\(^10,11\) Among the transitional metal oxides/hydroxides, iron oxides/hydroxides are the most attractive materials for the construction of the negative electrodes of supercapacitors owing to

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Iron oxides and hydroxides have different phases because of the different oxidation states of iron, which include FeO, FeO_2, Fe_2O_3, Fe(OH)_2, Fe(OH)_3, and FeOOH. Among these, FeOOH, Fe_2O_3, and Fe_3O_4 are the three most stable phases, and they have been extensively investigated as potential electrode materials for supercapacitors. Figure 1 summarizes the most common crystal structures of FeOOH, Fe_2O_3, and Fe_3O_4.

Figure 1. The most common crystal structures of FeOOH, Fe_2O_3, and Fe_3O_4.
tetrahedral sites and Fe$^{3+}$ ions only occupy the octahedral sites.$^{[28]}$

The electrochemical properties of iron oxides/hydroxides are highly dependent on their crystal structures, defect chemistry, morphology, porosity, and textures. Therefore, a good understanding of the influence of these structural parameters on the supercapacitor performance of iron oxides/hydroxides could set the basis for a rational design of advanced electrode materials. Iron oxides/hydroxides are promising anode materials for asymmetric supercapacitors; however, the specific capacitance of the conventional bulk powders is still low, which has constrained the further improvement in the energy density of supercapacitors. Such a challenging issue could be largely addressed by reducing the size of iron oxides/hydroxides into the nanoscale size regime, and there are a number of successful attempts in developing high-performance nanostructured iron oxide/hydroxide-based electrodes.$^{[29–35]}$ In particular, compared with the bulk materials, a larger surface area and a shorter diffusion length for ions could be readily created by nanoscale materials, which could improve the utilization efficiency of the electrode materials, leading to a significant increase in the specific capacitance and electrode performance of the as-designed electrodes.

The second limitation of iron oxides/hydroxides (except Fe$_3$O$_4$) is their relatively poor electrical conductivity, which might cause a large internal resistance (IR) drop and severe capacitance decline, particularly at a fast charge/discharge rate. Such a limitation requires addressing in the system of high-performance electrode materials.$^{[12–14]}$ Recently, there have been a number of successful attempts to improve the poor electrode kinetics of supercapacitors. Chemical modifications of iron oxides/hydroxides,$^{[12,36]}$ and integration of another highly conductive component (e.g., carbon nanotubes and graphene) into iron oxides/hydroxides$^{[37,38]}$ are two efficient strategies. Iron oxide/hydroxide-based electrode materials, either fabricated as a single nanostructured component with desirable physicochemical properties or integrated with a certain conductive material in the form of nanocomposites, provide a good platform to build high-performance electrodes for supercapacitors. This Focus Review aims to discuss and provide a scientific basis for the rational design of high-performance negative electrodes for asymmetric supercapacitors. We first summarize recent advances in developing iron oxide/hydroxide-based electrode materials, highlighting some important achievements in the field and providing some in-depth discussions of the design principles and mechanistic studies on the electrode materials. We then discuss three important strategies to design the electrode materials with improved energy density, which include architectural design, chemical modification, and multifunctional composites. In the last section, we point out some key challenges in materials design, which may require concerted efforts from the community, shedding some light on the design of electrodes for supercapacitors in both basic and applied research.

2. Electrochemical Behavior and Mechanistic Studies on Charge Storage in Iron Oxide/Hydroxide-Based Electrodes

Aqueous electrolytes are generally used in systems with iron oxide/hydroxide-based electrode materials, and this review will not cover the use of ionic liquids and organic electrolytes as they are only rarely used in the set-up.$^{[29]}$ Neutral (e.g., Na$_2$SO$_4$) or alkaline aqueous electrolytes (e.g., KOH) are normally used in the set-up for iron oxide/hydroxide-based electrodes, while acidic electrolytes are not commonly used owing to the highly corrosive nature of the acids. Although iron oxides/hydroxides have different crystal forms and compositions, they generally show a similar cyclic voltammetry (CV) behavior in both neutral and alkaline aqueous electrolytes. However, the CV behavior of the electrodes is largely dictated by the potential window used, as shown in Figure 2a. Most of the reported studies used a potential window of 0 to $-0.8$ V (vs. Ag/AgCl), and observed nearly rectangular CV curves without clear redox peaks. The pseudocapacitance in this potential region was considered to originate from the redox reaction between Fe$^{3+}$ and Fe$^{2+}$. For example, Chen et al.$^{[39]}$ performed an in-situ X-ray absorption spectroscopy (XAS) study on the FeOOH electrode ($\gamma$-FeOOH nanosheets) tested in a 1 M Li$_2$SO$_4$ electrolyte between 0 and $-0.8$ V (vs. Ag/AgCl). The XAS data provide supportive evidence for the reversible conversion between Fe$^{3+}$ and Fe$^{2+}$.

![Figure 2](image_url)

Figure 2. (a) Typical CV curves of a FeOOH/graphene composite electrode in different potential windows at a scan rate of 100 mV s$^{-1}$. (b) Rate performance and cycle performance of a FeOOH/graphene composite electrode in different potential windows. Reproduced with permission from ref. [13]. Copyright 2016, John Wiley and Sons.
However, when a lower cutoff potential was used (i.e., below −1.0 V vs. Ag/AgCl), the shape of the CV curve was significantly changed, and a pair of redox peaks were clearly seen. More recently, Liu et al.\(^{[46]}\) reported a detailed mechanistic study by using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), and their data clearly indicate the formation of metallic Fe\(^{0}\) when a Fe\(_2\)O\(_4\) electrode was discharged to −1.3 V (vs. Ag/AgCl) in a 3 m KOH electrolyte. This study also suggests that a deeper redox reaction occurs between Fe\(^{3+}\) and Fe\(^{0}\) in a broadened potential window.

Although different charge storage mechanisms have been proposed for the as-designed iron oxide/hydroxide-based electrodes for supercapacitors, the origin of pseudocapacitance and the exact faradaic reactions involved in the charge/discharge processes are still not fully understood. There have been some successful attempts. For example, according to the findings for Ni–Fe alkaline aqueous batteries, Fan et al.\(^{[33]}\) summarized the oxidation reactions of iron oxide/hydroxide-based anodes in alkaline electrolytes as follows:

\[
\begin{align*}
\text{Fe} + 2\text{OH}^- & \leftrightarrow \text{Fe(OH)}_2 + 2e^- \quad (E^0 = -1.076 \text{ V vs. SCE}) \tag{1} \\
3\text{Fe(OH)}_2 + 2\text{OH}^- & \leftrightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O} + 2e^- \quad (E^0 = -0.859 \text{ V vs. SCE}) \tag{2} \\
\text{Fe(OH)}_2 + \text{OH}^- & \leftrightarrow \text{FeOOH} + \text{H}_2\text{O} + e^- \quad (E^0 = -0.756 \text{ V vs. SCE}) \tag{3}
\end{align*}
\]

or/and

\[
\text{Fe(OH)}_2 + \text{OH}^- \leftrightarrow \text{FeOOH} + \text{H}_2\text{O} + e^- \quad (E^0 = -0.756 \text{ V vs. SCE}) \tag{3}
\]

It should be noted that similar redox peaks were observed for iron oxide/hydroxide-based electrodes in neutral aqueous electrolytes, regardless of the cations (e.g., Li\(^+\), Na\(^+\), or K\(^+\)) and anions (e.g., SO\(_4^{2-}\) or Cl\(^-\)) involved.\(^{[36,41,42]}\) These data suggest that the cations could be incorporated into the redox reactions of the electrode materials. The following is one possible reversible reaction for iron oxide/hydroxide-based electrodes in a neutral aqueous electrolyte.

\[
\text{FeO}_x + y\text{M}^+ + ye^- \leftrightarrow \text{M}_x\text{FeO}_y (\text{M = Li, Na, or K}) \tag{4}
\]

On the other hand, the exact faradaic reactions of iron oxides/hydroxides in either alkaline or neutral aqueous electrolytes are still not clear and need further investigation. Nevertheless, when the iron oxide/hydroxide-based electrodes were tested in the narrow potential window of −0.8–0 V (vs. Ag/AgCl), their CV behaviors were similar to those of double-layer capacitive materials (i.e., no clear redox peaks along with an excellent cycling stability but a low specific capacitance). In stark contrast, if a broad potential window (e.g., −1.3–0 V vs. Ag/AgCl) was applied, their CV behaviors were more like those in batteries, where well-defined redox peaks and large specific capacitance were often observed, together with a poor cycling stability and rate capability.\(^{[13,14,29,43–54]}\) For example, recent work by Xia’s group observed a fast capacitance fading in a FeOOH/graphene composite electrode, which was attributed to the dissolution of iron into the electrolyte when the system was operated in a potential window of −1.25–0 V (vs. Ag/AgCl, Figure 2b).\(^{[13]}\) In particular, the deep ion intercalation/de-intercalation in the host material caused a severe volume change, leading to deterioration in the mechanical stability of the electrode. Further approaching to a more negative potential will also accelerate the generation of H\(_2\) at the electrode, and the associated H\(_2\) bubbles generated at the current collector might further induce the peeling off of the active material. Therefore, although it is attractive in achieving a large specific capacitance in the broad potential window, the compromise in cycling stability makes the implementation of a broad potential window for iron oxide/hydroxide-based electrodes less practical for supercapacitors.

Na\(_2\)SO\(_4\) is an exception among the neutral aqueous electrolytes, in which the iron oxide/hydroxide-based electrodes showed different CV behaviors from those observed in other neutral or alkaline electrolytes. A number of studies have reported the electrochemical properties of iron oxide/hydroxide-based electrodes in Na\(_2\)SO\(_4\) electrolyte, which could achieve a specific capacitance in the range 100 to 300 F g\(^{-1}\).\(^{[34,47,55–59]}\) For example,\(^{[47]}\) a couple of redox peaks were seen in the CV curve of a Fe\(_2\)O\(_3\) electrode in Na\(_2\)SO\(_4\) electrolyte, which were attributed to the redox reactions that involved SO\(_4^{2-}\), including:

\[
\begin{align*}
2\text{SO}_4^{2-} + 3\text{H}_2\text{O} + 4e^- & \leftrightarrow \text{S}_2\text{O}_7^{2-} + 6\text{OH}^- \tag{5} \\
\text{S}_2\text{O}_7^{2-} + 3\text{H}_2\text{O} + 8e^- & \leftrightarrow 2\text{S}^{2-} + 6\text{OH}^- \tag{6}
\end{align*}
\]

The previous studies suggest that the pseudocapacitance was generated from the redox reactions of anions at the surface of the Fe\(_2\)O\(_3\) electrode, with no clear structural changes of the Fe\(_2\)O\(_3\) electrodes.\(^{[42]}\) Despite very limited studies on the use of Na\(_2\)SO\(_4\) electrolyte, the anion-involved faradaic reactions in metal oxide-based electrodes are very interesting and could provide a good platform to further improve the electrochemical performance of the pseudocapacitive electrode materials.

It should be noted that the use of iron oxide/hydroxide-based electrodes in a positive potential window in either neutral or alkaline aqueous electrolytes has been attempted less.\(^{[60–63]}\) In particular, the advantages of using iron oxides/hydroxides as cathode materials for supercapacitors are not clear compared with other potential cathode materials such as NiO/ Ni(OH)\(_2\), and Co\(_3\)O\(_4\)/Co(OH)\(_2\). Therefore, in this review we will not include a discussion of the iron oxide/hydroxide-based cathodes for supercapacitors.

### 3. Architectural Design in Nanostructured Iron Oxides/Hydroxides

Recently, nanostructured iron oxides/hydroxides have attracted great interest in the community owing to their superior electrochemical performance over their conventional bulk counterparts.\(^{[8,9]}\) It is well known that the morphology and porosity of the electrode play an important role in the capacitive performance of supercapacitors. Recent studies have shown that the capacitive performance could be significantly improved by...
reducing the size of the active materials to the nanoscale, as nanostructured materials feature increased accessible surface area and shortened paths for charge transport compared with their bulk counterparts. To date, various nanostructures, including zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) nanostructures, have been successfully fabricated for iron oxides/hydroxides. A number of synthesis methods, including electrochemical deposition, sol-gel methods, thermal decomposition, hydrothermal/solvothermal methods, template-based methods, microwaves-assisted methods, and electrochemical anodization, have been developed to prepare nanostructured iron oxides/hydroxides with well-defined size and morphology. In this section, we provide a detailed survey of the use of iron oxides/hydroxides with different shapes for the construction of anodes for supercapacitors.

3.1. 0D nanostructures

Spherical nanoparticles are the most common 0D nanostructures (Figure 3a), and they can be synthesized in a relatively easy way compared with nanomaterials of other architectures. For instance, FeOOH nanoparticles can be obtained by the hydrolysis of inorganic iron salts in an aqueous solution. The particle size, crystalline phase, and morphology can also be controlled by the reaction conditions, including salt concentration, organic additives, pH, and synthesis temperature. For example, Xue et al. reported a successful synthesis of FeOOH nanoparticles with different morphologies and sizes by using different iron salts, such as FeSO₄, FeCl₂, FeCl₃, and Fe(NO₃)₃. Based on the hard–soft acid–base theory, the anions could be used to control the chemical reaction and crystallization process of FeOOH. The as-prepared FeOOH nanoparticles exhibited high specific capacitances in a range 440 to 620 F g⁻¹ at a potential of −1.2 to 0 V (vs. Ag/AgCl) and a current density of 1 A g⁻¹. Calcination of FeOOH nanoparticles in air will convert them to Fe₂O₃ nanoparticles.

Fe₂O₃ nanoparticles are often prepared by hydrothermal or sol-gel methods, and the latter is generally more suitable for mass production. For example, Shivakumara et al. reported a sol-gel method to prepare α-Fe₂O₃ nanoparticles with small particle size (∼5–15 nm, Figure 3b) and large surface area (∼386 m² g⁻¹). The as-prepared Fe₂O₃ nanoparticles can deliver a specific capacitance of ~300 F g⁻¹ between −0.8 and 0 V (vs. Ag/AgCl) at a current density of 1 A g⁻¹. It should be mentioned that a Fe²⁺/Fe³⁺ molar ratio of 0.5 was generally used to prepare the Fe₂O₃ nanoparticles. However, the easy aggregation of magnetic Fe₃O₄ nanoparticles might result in large particle size and low specific surface area. Recently, Wang et al. reported a facile ultrasonic synthesis of Fe₂O₃ nanoparticles (Figure 3c) by using FeCl₃ and an organic solvent—ethanolamine. The as-prepared Fe₂O₃ nanoparticles possessed a high specific surface area of 165 m² g⁻¹ and could deliver a large specific capacitance of 207.7 F g⁻¹ between −0.9 and 0.1 V (vs. Ag/AgCl) at a current density of 0.4 A g⁻¹ in a 1 M Na₂SO₄ electrolyte.

Figure 3. (a, d, g, and j) Schematic illustration of 0D, 1D, 2D, and 3D nanostructures. (b) TEM image of Fe₂O₃ nanoparticles synthesized by a sol-gel method. Reproduced with permission from ref. [68]. Copyright 2016, Elsevier. (c) TEM image of Fe₂O₃ nanoparticles synthesized by a hydrothermal method. Reproduced with permission from ref. [32]. Copyright 2015, Royal Society of Chemistry. (e) SEM image of FeOOH nanorods synthesized by a hydrothermal method. Reproduced with permission from ref. [32]. Copyright 2015, Royal Society of Chemistry. (f) SEM image of Fe₂O₃ nanotubes synthesized by a template-assisted method. Reproduced with permission from ref. [46]. Copyright 2014, American Chemical Society. (h, i) SEM and TEM images of Fe₂O₃ nanosheets grown on a nickel foil by a hydrothermal method. Reproduced with permission from ref. [35]. Copyright 2015, Royal Society of Chemistry. (k, l) SEM and TEM images of Fe₂O₃ hollow microspheres synthesized by a solvothermal method in an ionic liquid. Reproduced with permission from ref. [64]. Copyright 2016, Royal Society of Chemistry.

3.2. 1D nanostructures

1D nanostructures of iron oxides/hydroxides, such as nanorods, nanowires, and nanotubes (Figure 3d), have also attracted great interest in the community as the 1D nanostructures feature an efficient electrode–electrolyte contact owing to their large surface-to-volume ratio, efficient 1D electron transport, and facile strain relaxation during the ion intercalation. 1D nanorods and nanowires of iron oxides/hydroxides are generally prepared by a hydrothermal method. For example, Xue et al. reported a hydrothermal method to prepare FeOOH nanorods (Figure 3e) with different morphologies and sizes by simply controlling the Fe³⁺ concentration. It was shown that the FeOOH nanorods with a smaller diameter exhibited a larger specific capacitance. The optimized electrode can reach a large specific capacitance of 714.8 F g⁻¹ between −1.2 and 0 V (vs. Ag/AgCl) at a current density of 1 A g⁻¹ in a 2 M KOH electrolyte. Similarly, by using a lower synthesis temperature of 60 °C in the hydrothermal reaction, Wang et al. have successfully prepared ultrafine Fe₂O₃ nanowires with a diameter of 10 nm on carbon cloth, and this material...
could achieve a large specific capacitance of approximately 908 F g⁻¹ between −1.35 and 0 V (vs. Ag/AgCl) at a current density of 2 A g⁻¹ in a 2 M KOH electrolyte.

Electrochemical anodization is an effective method to produce nanotubular structures, and it has been successfully used to prepare iron oxide nanotubes on an iron substrate.³⁴,³⁷,³⁸ Nanotubes can also be prepared by using a template method. For example, Yang et al.⁴⁶ synthesized Fe₃O₄ nanotubes (Figure 3f) on carbon cloth by using ZnO nanorods as the template in a wet chemical synthesis. The as-prepared Fe₃O₄ nanotube arrays can deliver a large specific capacitance of approximately 257.8 F g⁻¹ as well as a good rate performance, which can be attributed to the nanotubular morphology featuring a large interfacial area and shortened diffusion path for ions.

3.3. 2D nanostructures

Similar to 1D nanostructures, 2D nanostructures such as nanosheets and nanoflakes (Figure 3g) are also beneficial for achieving large surface area, shortened ion diffusion paths, and improved structural stability. Recently, 2D nanosheets with one or several layers of atoms or crystallites have been extensively investigated in the field as a new class of functional nanomaterials.³⁴ For example, γ-FeOOH nanosheets have been prepared on carbon fiber substrates by a simple one-step electrophoretic method without the assistance of any template or surfactant.³⁴ The optimum specific capacitance of the as-synthesized γ-FeOOH nanosheets was 310.3 F g⁻¹ between −0.8 and 0 V (vs. Ag/AgCl) at a current density of 0.13 A g⁻¹ in a 1 M Li₂SO₄ electrolyte. The as-designed electrode also has a large energy density of 29.8 Wh kg⁻¹ at a high power density of 9000 W kg⁻¹, which indicates that the 2D layered channels of γ-FeOOH nanosheets could facilitate fast penetration of the electrolyte and rapid electron transfer for charge storage and delivery. More recently, both Fe₃O₄ and Fe₃O₄ nanosheet arrays (Figure 3h,j) have been successfully fabricated on a Ni foam substrate by a hydrothermal method.³⁶,³⁷ The Fe₃O₄ nanosheet arrays delivered a large specific capacitance of approximately 379.8 F g⁻¹ between −1 and 0 V (vs. SCE) at a current density of 2 A g⁻¹ in a 2 M KOH electrolyte. The good performance of the as-designed electrode was attributed to the good electrical conductivity and the porous structure of the Fe₃O₄ nanosheets. Nanoflakes are another attractive architecture of iron oxides/hydroxides. For example, Liu et al.⁵⁰ reported the synthesis of ultra-thin Fe₃O₄ nanoflakes through an electrochemically induced morphological transformation of Fe₃O₄ nanorods. The as-prepared Fe₃O₄ nanoflakes exhibited an improved capacitive performance compared with the original Fe₃O₄ nanorods largely owing to the increased surface area and reduced charge transfer resistance in the nanoflakes. These studies have exemplified the good designs of high-performance iron oxide/hydroxide-based electrodes for supercapacitors.

3.4. 3D nanostructures

In general, 3D porous nanostructures (Figure 3j) have a large surface area, and they also feature good durability in the process of ion intercalation/de-intercalation at high current densities because the 3D porous structures can efficiently accommodate large volume change and facilitate fast charge transport.¹¹,⁶⁴,⁷³ In particular, incorporation of porosity into micro-meter-sized (or microscale) particles is an efficient morphology design, as porous microparticles have adequate particle sizes and good particle–particle contacts, and they could also maximize the rate capability by reducing the diffusion path. Therefore, an efficient method to prepare 3D porous structures or microscale/nanoscale hybrid structures is desirable for constructing electrode materials for high-performance supercapacitors. For example, Fu et al.⁶⁴ reported the synthesis of hollow and porous Fe₃O₄ microrods (Figure 3k,l) by using a facile and scalable chemical treatment of mill scale—a waste product from the steel industry. This 3D porous/hollow structure effectively improved the electrochemical performance, resulting in a large specific capacitance of approximately 346 F g⁻¹ at a scan rate of 2 mV s⁻¹ between −1 and 0 V (vs. Ag/AgCl) in a 0.5 M Na₂SO₄ electrolyte. Another salient point of using mill scale as a precursor to prepare Fe₃O₄ electrode materials is its low cost per unit energy/power compared with a similar material synthesized from high-purity chemical precursors. This feature is very attractive for large-scale energy storage applications.

4. Iron Oxide/Hydroxide-Based Composites

Although reducing the particle size to the nanoscale is effective in improving the capacitive performance of iron oxide/hydroxide-based electrodes, the improvement is still limited and the as-designed electrodes are not yet competitive compared with other competing technologies. For nanoparticles, aggregation often occurs during the electrode preparation and charge/discharge cycling, and the aggregation of active materials will reduce the accessible interface area, thus compromising their capacitive performance.⁴⁶ Another key issue for iron oxide/hydroxide-based electrodes is their poor electrical conductivity, which could reduce the specific capacitance at a high charge/discharge rate.¹²,¹³ Incorporating another functional material with high conductivity is a promising solution to address the issue of poor electrical conductivity in iron oxide/hydroxide-based electrode materials. A delicate design of multifunctional iron oxide/hydroxide-based composites may significantly boost their capacitive performance compared with the electrode materials with a single component.

4.1. Iron oxide/hydroxide–carbon composites

To improve electron transport in the electrode and suppress the aggregation of nanomaterials, carbon materials such as carbon nanotubes (CNTs)¹⁷,¹⁰,⁷⁸–⁸⁰ graphene,⁸¹–⁹¹ porous carbon,⁹⁴–⁹⁶ and coated thin carbon layers,⁴⁶,⁹⁷ are commonly used as conductive additives for iron oxide/hydroxide-based electrode materials largely because of their large surface areas and good electrical conductivity. For example, CNTs have been used as promising double-layer capacitive electrode materials for supercapacitors owing to their excellent electrical conductivity, unique pore structure, and exceptional mechanical,
Recently, hybrid electrode composites consisting of conductive CNTs (as an interconnected 3D porous network) and metal oxide nanoparticles (with rapid surface faradaic reactions) have been developed to improve the energy and power density of supercapacitors. According to a recent study by Cho et al.,[37] uniform incorporation of the metal oxide nanoparticles into the CNT conducting matrix is crucial for the preparation of high-performance electrodes. For example, ultrathin CNT/FeOx nanocomposite electrodes were prepared by a layer-by-layer (LBL) assembly of the amine-functionalized CNTs and oleic acid-stabilized FeOx nanoparticles, making use of the electrostatic interactions between the amine and carboxylic groups. The data suggest that the composite electrodes can largely minimize the internal interfacial resistance by the strong electrostatic-interaction-induced adsorption of densely packed and high-quality FeOx nanoparticles onto CNTs, without the use of binders or insulating ligands; such a delicate design has significantly improved the volumetric capacitance and cycling stability of the electrodes. As shown in Figure 4a–c, Guan et al.[79] used graphene foam-supported CNTs (GF-CNT) as the conductive matrix and coated FeOx nanoparticles on the CNT surface by atomic layer deposition (ALD). The as-obtained CNT/FeOx composite has a core–shell structure, and showed an improved rate capability (Figure 4d) and cycling stability, which can be attributed to the large surface area and fast charge transport in the as-designed electrodes. More recently, several new types of freestanding carbon-based 3D architectures including aerogel, foams, and sponges have shown further improved mechanical properties for the electrodes,[79] and they could find potential applications in flexible energy storage devices. For example, Cheng et al.[102] reported the preparation of a 3D FeOx/CNT sponge electrode with a porous hierarchical structure with FeOx nanohorns anchored on the surface of CNTs (Figure 4e–g). The hybrid sponges exhibited a large specific capacitance of ~300 F g⁻¹ at a scan rate of 5 mV s⁻¹ between −1 and 0 V (vs. Ag/AgCl) in a 2 M KCl electrolyte. They also showed a good rate performance and high flexibility (Figure 4h), which has potential for the application of light-weight and flexible energy storage devices.

Graphene is a rising star in the carbon community. It has a unique 2D layered structure, and has triggered an exciting new era in the field of carbon nanoscience with ever-increasing scientific and technological impetus. Graphene has a large theoretical surface area of 2630 m² g⁻¹, high conductivity, excellent chemical and thermodynamic stability, and lightweight characteristics, making it an ideal conductive matrix for developing high-performance iron oxide/hydroxide-based composites for supercapacitors.[81] A number of studies on iron oxide/hydroxide-graphene composites have been reported,[81–90] demonstrating significantly improved capacitive performance compared with that of the individual iron oxides/hydroxides. Perfect graphene is seldom used directly as the starting material to combine with iron oxide/hydroxide particles owing to its poor dispersibility in most solvents and weak interaction with metal oxides, resulting from limited functional groups on the surface.[49] For the synthesis of iron oxide/hydroxide–graphene composites, graphene oxide (GO) nanosheets, a precursor of graphene, are commonly used as the starting material because the rich functional groups on GO can function as active sites to bind the Fe ions.[88–91] An ex-situ synthetic route by simply mixing metal oxides with graphene or GO can only establish a weak interaction between the two components, which leads to severe aggregation of the metal oxide particles with a subsequent degradation of electrochemical performance.[90] Directly growing iron oxide/hydroxide particles on
Furthermore, it is worth mentioning that the mesocrystal/graphene anode composites by self-assembly of FeOOH nanoparticles as the primary building blocks on graphene under hydrothermal conditions, followed by a concomitant phase transition from FeOOH to Fe$_2$O$_3$ (Figure 5a,b). The Fe$_2$O$_3$/graphene composite obtained by slow annealing had a large specific surface area of 95.9 m$^2$g$^{-1}$ and delivered a large specific capacitance of $\approx$ 343.7 F g$^{-1}$ between −1 and 0 V (vs. Ag/AgCl) at a current density of 3 A g$^{-1}$ in a 1 M Na$_2$SO$_4$ electrolyte (Figure 5c), which can be ascribed to the intrinsic characteristics of the mesoscopic structure of Fe$_2$O$_3$ nanocrystals and the crumpled graphene, facilitating charge transport at the interface. To obtain large specific capacitance, Xia et al.,$^{[13]}$ adopted another strategy to minimize the particle size of Fe$_2$O$_3$ on graphene. In their work, a one-step thermal decomposition method was developed to synthesize Fe$_2$O$_3$ quantum dots (QDs, ~2 nm) decorated on functionalized graphene sheets (FGS; Figure 5d,e) at a low temperature of 200 °C. It has been found that the Fe$_2$O$_3$/FGS mass ratio in the composites plays an important role in determining the supercapacitive performance of the composite electrodes. The optimized Fe$_2$O$_3$/FGS composite electrode can reach a large specific capacitance of $\approx$ 347 F g$^{-1}$ between −1 and 0 V (vs. Ag/AgCl) at a scan rate of 10 mV s$^{-1}$ in a 1 M Na$_2$SO$_4$ electrolyte as well as excellent rate capability (Figure 5f). As shown in Figure 5g–i, the Fe$_2$O$_3$/FGS composite electrode was coupled with a MnO$_2$/FGS composite electrode to construct a 2 V asymmetric supercapacitor with a high energy density of 50.7 Wh kg$^{-1}$ at a power density of 100 W kg$^{-1}$. The facile synthesis method and the superior electrochemical performance make Fe$_2$O$_3$/FGS/MnO$_2$/FGS asymmetric supercapacitors promising for applications in high-performance energy storage systems.

4.2. Iron oxide/hydroxide–polymer composites

Conducting polymers, such as polyaniline (PANI), poly(3,4-ethylenedioxythiophene) (PEDOT), and polypyrrole (PPy), are considered as a class of additive materials to couple with metal oxides owing to their relatively high electronic conductivity, ease of preparation, and ultrahigh stability.$^{[84–102]}$ To enhance the cycle life and rate capability of nanostructured iron oxide/hydroxide electrodes, polymer coating is usually employed for developing the composites because the polymer not only acts as a flexible buffering layer to prevent the structure from destruction/degradation, but also increases the conductivity of the electrodes. Recently, Li et al.$^{[103]}$ reported a PANI-coated α-Fe$_2$O$_3$ core–shell nanowire (Figure 6a) on carbon cloth by an electrodeposition method. The α-Fe$_2$O$_3$/PANI composite electrode achieved a high areal capacity of 103 mF cm$^{-2}$ between −0.8 and 0 V (vs. SCE) at a current density of 0.5 mA cm$^{-2}$, which is twice of that for the pure α-Fe$_2$O$_3$ electrode (33.93 mF cm$^{-2}$, Figure 6b). Moreover, the α-Fe$_2$O$_3$/PANI electrode showed excellent structural stability with almost 100% capacity retention after 2500 cycles as a result of the protective PANI shell (Figure 6c). Alternatively, Hao et al.$^{[104]}$ reported the synthesis of graphene/Fe$_2$O$_3$/PANI composites by an in-situ chemical polymerization of aniline in a graphene/Fe$_2$O$_3$ suspension. By coating the graphene/Fe$_2$O$_3$ nanosheets with a thin PANI layer (Figure 6d,e), the composite electrode showed a high specific capacitance of 638 F g$^{-1}$ between −1 and 0 V (vs. SCE) at a scan rate of 1 mV s$^{-1}$ in a 1 M KOH electrolyte (Figure 6f). Moreover, the ternary composite electrode has also exhibited excellent cycling stability with a capacitance decrease of only 8% after 5000 cycles. Taking advantage of the synergistic effects of the hybrid structures, the ternary composite electrode showed an enhanced energy of 107 Wh kg$^{-1}$ at a power density of 351 W kg$^{-1}$, and 17 Wh kg$^{-1}$ even at a higher power density of 4407 W kg$^{-1}$.

4.3. Other composites

In addition to carbon and conductive polymers, iron oxides/hydroxides have also been combined with other materials to develop iron oxide/hydroxide...
composites with improved electrochemical performance for supercapacitors. For example, Liu et al.\textsuperscript{[104]} reported a hybrid Fe\textsubscript{3}O\textsubscript{4}@SnO\textsubscript{2} core–shell nanorod film grown directly on a Ti substrate (Figure 7a,b). The combination of the conductive Fe\textsubscript{3}O\textsubscript{4} core and porous SnO\textsubscript{2} shell has enabled the composite to achieve a much higher areal capacitance of 7.013 mF cm\textsuperscript{-2} compared with the pristine Fe\textsubscript{3}O\textsubscript{4} nanorod film at a current density of 0.20 mA cm\textsuperscript{-2} between 0.8 and −0.2 V in a 1 M Na\textsubscript{2}SO\textsubscript{4} electrolyte (Figure 7c), demonstrating an effective approach to integrating different metal oxides into one intriguing architecture to greatly enhance the capacitive performance. By adopting the similar conductive core–large capacitance shell structure, recently, Xia’s group\textsuperscript{[53]} constructed hierarchichal Fe\textsubscript{3}O\textsubscript{4}@SnO\textsubscript{2} core–shell nanorod arrays on a Ti substrate (Figure 7d,e). Compared with the bare Fe\textsubscript{3}O\textsubscript{4} and Fe\textsubscript{3}O\textsubscript{4} nanorod arrays, the hybrid Fe\textsubscript{3}O\textsubscript{4}@SnO\textsubscript{2} nanorod arrays exhibited a much larger volumetric capacitance up to 1206 F cm\textsuperscript{-3} between −1 and 0 V (vs. Ag/AgCl) at a scan rate of 5 mV s\textsuperscript{-1} in a 1 M Na\textsubscript{2}SO\textsubscript{4} solution together with good rate capability (Figure 7f).

5. Intrinsic Modifications of Iron Oxides/Hydroxides

Besides the extrinsic modifications of the iron oxides/hydroxides, intrinsic modifications, including the introduction of oxygen vacancies, control of crystallinity and crystal structure, and foreign ion doping, have also been demonstrated to be effective ways to tailor the electronic properties and chemical reactivity of iron oxides/hydroxides and consequently tune their capacitive performance. The introduction of oxygen deficiencies in transition metal oxides is considered as an impactful strategy to enhance the intrinsic conductivity, resulting in a great enhancement in the electrochemical performance.\textsuperscript{[105,106]} Recently, Lu et al.\textsuperscript{[12]} have reported an oxygen-deficient α-Fe\textsubscript{3}O\textsubscript{4} nanorod (N-Fe\textsubscript{3}O\textsubscript{4}) grown on a carbon cloth by a simple thermal treatment of the as-prepared FeOOH nanorods in a N\textsubscript{2} atmosphere. The oxygen vacancy causes uneven d-spacing and the zigzag arrangement of the lattice fringes (Figure 8a) with the generation of a certain amount of Fe\textsuperscript{2+} in α-Fe\textsubscript{3}O\textsubscript{4} (Figure 8b). It is noted that the oxygen-deficient N-Fe\textsubscript{3}O\textsubscript{4} nanorods achieved a remarkable enhancement of areal capacitance as well as much better rate performance compared with the defect-free A-Fe\textsubscript{3}O\textsubscript{4} (Figure 8c), which can be attributed to the improved electrical conductivity and the increased active sites at the surface.

Most research on iron oxides/hydroxides has focused on the crystalline rather than the amorphous phase. The amorphous materials, however, have recently been demonstrated to be promising electrode materials for energy storage.\textsuperscript{[107,108]} Compared with crystalline materials with similar particle size and morphology, amorphous materials could have faster electrode kinetics owing to isotropic ion diffusion and more percolation pathways and homogeneous expansion and contraction due to the isotropic nature. For example, recently, Xia’s group\textsuperscript{[13]} reported the synthesis of amorphous FeOOH QDs/graphene hybrid nanosheets (Figure 8d,e) and investigated their electrochemical performance as negative electrode materials for supercapacitors (Figure 8f). Interestingly, the amorphous FeOOH QDs/FGS electrode exhibited a large specific capacitance of 365 F g\textsuperscript{-1} between −0.8 and 0 V (vs. Ag/AgCl) in a 1 M Li\textsubscript{2}SO\textsubscript{4} electrolyte, an excellent rate capability (189 F g\textsuperscript{-1} at a current density of 128 Ag\textsuperscript{-1}), and an outstanding cycle performance (89.7% capacitance retention after 20 000 cycles), significantly outperforming the crystalline iron oxide/hydroxide-based electrode materials. This work provides new opportunities for developing
high-performance electrode materials for supercapacitors, especially for amorphous electrode materials.

Foreign ion doping is a widely used method for metal oxides to improve the intrinsic electrical conductivity. Recently, Lu et al.\textsuperscript{[36]} reported Ti-doped Fe$_3$O$_4$ nanorods (Figure 8 g,h) synthesized by a hydrothermal method. It was found that the doping of Ti in the Fe$_3$O$_4$ electrode led to a larger surface area and enhanced electrical conductivity, resulting in considerably increased specific capacitance compared with the pristine Fe$_3$O$_4$ electrode (Figure 8 i). Alternatively, Yu et al.\textsuperscript{[110]} reported F-doped β-FeOOH nanorods grown on a carbon cloth. Theoretical calculations showed that the F doping in β-FeOOH will significantly reduce the band gap of FeOOH and thus increase the conductivity. Experimental results confirmed that the F-doped β-FeOOH possessed metal-like high electrical conductivity with greatly improved capacitive performance.

6. Conclusions and Perspectives

In summary, iron oxide/hydroxide-based materials are a class of promising anode materials for asymmetric supercapacitors using aqueous electrolytes. The electrochemical behavior of iron oxide/hydroxide-based electrodes is highly dependent on the potential window. In particular, double-layer capacitive behavior is observed in the narrow potential window of −0.8 to 0 V (vs. Ag/AgCl), whereas a pseudocapacitive behavior is observed in the broad potential window of −1.3 and 0 V (vs. Ag/AgCl). Although the complete faradaic reaction between Fe$^{3+}$ and Fe$^{2+}$ could lead to a much larger specific capacitance, the compromise of poor cycling stability and low rate capability retards the practical application of these materials in the broad potential window. The charge storage mechanism of iron oxide/hydroxide-based materials in either alkaline or neutral aqueous electrolytes is still under debate. Nevertheless, the anion involved faradaic reaction could be a new direction for developing high-performance electrode materials for supercapacitors, considering both cations and anions could be utilized together for a single electrode to contribute to the pseudocapacitance.

Nanostructuring and architectural design is necessary for iron oxides/hydroxides to provide a large surface area that can enhance the utilization of the active material and increase the specific capacitance. Various nanostructures, including 0D, 1D, 2D, and 3D structures, are effective in increasing the surface area and shortening the ion diffusion path. Nanostructuring alone, however, cannot maximize the capacitive performance of iron oxides/hydroxides because intrinsic poor electrical conductivity is another obstacle that limits the charge storage capability especially at a high charge/discharge rate. The poor electrode kinetics can be improved either by an extrinsic route to make composites with conductive components or by an intrinsic route that tailors the conductive property of the material itself. The initial trial of nanostructured amorphous material suggests great potential for using amorphous iron oxide/hydroxide-based electrode materials for supercapacitors. Future research will focus on developing new strategies that can stabilize iron oxide/hydroxide-based electrode materials in a broad potential window to achieve higher energy density.

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