Iron anode-based aqueous electrochemical energy storage devices: Recent advances and future perspectives

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Abstract

The ever-growing demands for green and sustainable power sources for applications in grid-scale energy storage and portable/wearable devices have enabled the continual development of advanced aqueous electrochemical energy storage (EES) systems. Aqueous batteries and supercapacitors made of iron-based anodes are one of the most promising options due to the remarkable electrochemical features and natural abundance, pretty low cost and good environmental friendliness of ferruginous species. Though impressive advances in developing the state-of-the-art ferruginous anodes and designing various full-cell aqueous devices have been made, there still remain key issues and challenges on the way to practical applications, which urgently need discussing to put forwards possible solutions. In this review, rather than focusing on the detailed methods to optimize the iron anode, electrolyte, and device performance, we first give a comprehensive review on the charge storage mechanisms for ferruginous anodes in different electrolyte systems, as well as the newly developed iron-based aqueous EES devices. The deep insights, involving the inherent failure mechanisms and corresponding modification/optimization strategies toward iron anodes for the development of high-performance aqueous EES devices, will then be discussed. The advances in applying iron-based aqueous EES devices for emerging fields such as flexible/wearable electronics and functionalized building materials will be further outlined. Last, future research trends and perspectives for maximizing the potential of current iron anodes and devices as well as exploiting brand-new iron-based aqueous EES systems are put forward.

KEYWORDS
aqueous batteries, battolyser, charge storage mechanism, hybrid supercapacitors, iron anode
1 | INTRODUCTION

The giant combustion of fossil fuels for energy supply has globally raised environmental concerns on negative climatic changes (global warming, etc.) and air pollutions (photochemical smog, haze, acid rain, etc.).[11–30] Exploitation and widespread utilization of clear and renewable energy such as solar, wind and tide, thereby, becomes thriving and imperative to combat environmental deteriorations.[4] Nevertheless, the harvest for such natural energy is intermittent since its collection is generally impacted by complex/random factors (like geographic location, sunshine duration, capricious climate, etc.).[5–7] To make effective use of these sustainable energy sources and balance the grid during the peak-power demands, the development of large-scale and low-cost electrochemical energy storage (EES) systems undoubtedly plays a critical “enabler” role.[8] To date, both supercapacitors and batteries have dominated as popular EES devices due to their high charge-storage efficiency, outstanding cyclic durability and design diversity.[8–13] The commercialized carbon-based supercapacitors are generally featured by high power density (5–10 kW kg⁻¹) and ultra-long cyclic lifespan (>10⁶ cycles) but very limited energy density (<10 Wh kg⁻¹), which makes them unappealing for grid-scale EES applications.[11–14] Whereas, the commonly used batteries with energy densities ranging from 30 to 400 Wh kg⁻¹ may be competent as reliable EES devices.[15–26] For instance, lithium-ion batteries (LIBs) that are already widely applied in portable electronics, are deemed a promising choice to store the clean and sustainable energy.[17–19] However, the reserves shortage (only 13 million tons of Li remain in the earth’s crust according to recent US Geological survey) and ever-increasing consumptions for Li resources (the worldwide Li₂CO₃ demand annually increases ca. 7%–10%) propel human beings to seek for alternative sustainable and cost-effective rechargeable batteries without compromising the energy-storage efficiency and capacity.[20] In this regard, sodium- and potassium-ion batteries (SIBs and PIBs) with similar chemistry to LIBs have shown great promise considering the natural abundance of Na and K.[21–26] Nonetheless, their electrochemical performance in terms of energy density and capacity retention are usually inferior when compared with state-of-the-art LIBs.[23,25] For LIBs, SIBs, and PIBs, the reserves of transition metal (e.g., Co and Ni) minerals used to produce battery cathodes are also limited, making the mass fabrication cost dramatically increased. In addition, the organic electrolytes used in these batteries are typically toxic and volatile/flammable, easy to cause safety issues when cell modules suffer from short-circuit or work under extreme conditions.[27,28]

Benefiting from the use of water-based electrolytes, rechargeable aqueous EES devices have gained continuous attentions for a long period, despite that their energy density is intrinsically limited by the electrochemical stability window of water.[29–37] The involved aqueous electrolyte is abundant, eco-friendly to the environment, ionically conductive and truly safe (non-flammable), making the aqueous devices quite promising for use in large-scale energy storage. Therefore, in parallel with the continual progress of LIBs/SIBs/PIBs, various aqueous batteries such as zinc/nickel (Zn/Ni), zinc/manganese (Zn/Mn), bismuth/nickel (Bi/Ni), iron/nickel (Fe/Ni), iron/cobalt (Fe/Co), and titanium/nickel (Ti/Ni) have been extensively studied.[38–46] These batteries are generally operated in alkaline, acid, or neutral electrolyte solutions, with metal or metal oxide as the anode; the dominant charge storage mechanism at the anodic side is conversion-type reaction, which in principle contributes higher capacity as compared to intercalation/insertion anodes utilized in traditional aqueous LIBs/SIBs/PIBs. A higher energy density can therefore be expected. Among high-energy aqueous EES devices, iron-based ones have drawn tremendous attention owing to the following notable merits.[47] First, the Fe element is earth-abundant (the richest transition metal element in earth’s crust) and less toxic than other metallic counterparts.[48] Hence, the ferruginous species (e.g., Fe₃O₄, FeO, FeOOH, Fe, etc.) are rather cheap and readily available from either manufacturing or recycling, showing great promise in commercialization for large-scale EES.[49] Second, Fe possesses rich valence states (Fe⁰, Fe²⁺ and Fe³⁺) and multi-electron redox behaviors, endowing iron-based electrodes with a great specific energy.[50] Third, ferruginous materials are quite unique in terms of electrochemical characteristics; they have relatively good ability to restrict water hydrolysis (H₂ evolution), giving rise to a wide and stable working window at the negative potential range and thus increasing the operating voltage and energy density of aqueous devices.[51] Fourth, iron-based aqueous EES devices generally exhibit great tolerance to negative manipulations like over-charge/discharge, mechanical shock/vibration or even short-circuit. Furthermore, their good environmental friendliness and compatibility with intermittent energy sources make them competitive with other counterparts.

Despite the great merits mentioned above, the development of reliable iron-based aqueous EES devices is still challenging, mainly due to the issues of conventional ferruginous electrode materials: (i) unsatisfactory electronic conductivity of actives at the initial or intermediate states (hence causing a large internal potential drop) and (ii) inferior structural stability led by large...
volumetric expansions and structural deformation in repeated phase-change processes, giving rise to unsatisfied electrochemical performance (e.g., rate capability) and cyclic stability in contrast to currently dominant energy-storage devices.\cite{47} Till now, considerable efforts have been devoted to exploiting manifold iron-based species as anodes for aqueous EES devices, including batteries and battery-supercapacitor hybrid devices.\cite{52–58} However, challenges remain in addressing all the issues of iron anode with simple electrode design. In particular, the charge storage mechanism of iron anodes may be different in various aqueous EES devices, which gives rise to more specific issues that need to pay additional attention. Consequently, the anode design strategy and device assembly way have been demonstrated to be very diverse.

Given the recent giant increasing publications on iron-based anodes for aqueous EES applications, herein, we intend to review the most up-to-date progress in this fascinating research field (see the guide tree in Figure 1). This review will not simply summarize the methods of improving iron anode performance from the aspects of electrode architecture and electrolyte design.\cite{53–55} We will begin with the basic overview of reported charge-storage mechanisms of ferruginous anodes in different iron-based EES devices; the key challenges will be discussed in detail. Thereafter, the inherent failure mechanism of these iron anodes upon deep charging and discharging will be analyzed, followed by summing up the current major optimization strategies to benefit the implementation of iron-based aqueous devices for large-scale applications. The advances in designing iron-based EES devices for future flexible/wearable electronics and functional building materials will be further outlined. We end this review with perspectives and outlook, pointing out several feasible research trends (denoted as “four R”) and hoping it may shed new light in making advanced iron-based anodes and devices.

2 | Charge Storage Mechanism of Iron-Based Anode in Different Systems

2.1 | Conventional alkaline devices

Iron anode-based alkaline batteries are one of the most popular aqueous EES devices reported in literatures. During the past decades, there have been considerable efforts dedicated to the synthesis of ferruginous anodes for alkaline batteries. Those mainly includes Fe-VI group materials (e.g., FeO, Fe₂O₃, Fe₃O₄, FeS, FeS₂, FeSe, Fe(OH)₂, and Fe(OH)₃), the metallic Fe⁰ and other Fe-contained compounds (e.g., ZnFe₂O₄, CuFe₂O₄, MnFe₂O₄, and FeF₃).\cite{47–60} No matter the type of ferruginous species, the main electrochemical reaction involves the total or partial conversion between Fe-based anode material and Fe(OH)ₓ/FeOₓ/Fe on the anode surface, as schematically shown in Figure 2A (bottom-left). To generally illustrate their charge storage mechanisms, we have taken the simplest Fe anode as a case example, and the typical cyclic voltammogram (CV) scan is shown (bottom-right in Figure 2A). The possible involved electrochemical reactions are described as follows:
In the initial charge process (three-electrode mode), Fe actives are electrochemically oxidized into Fe(OH)$_2$ (Fe-to-Fe$^{(II)}$ oxidation, see its related O$_1$ peak). This reaction proceeds easily since Fe metals are apt to corrode in O$_2$-involved alkaline solutions. Particularly note that this oxidation reaction relies on the "dissolution−precipitation" mechanism with a soluble ferrite intermediate (HFeO$_2^−$).\[63\] Corresponding reactions are described below:

\[
\begin{align*}
\text{Fe} + 3\text{OH}^- &\leftrightarrow \text{HFeO}_2^- + \text{H}_2\text{O} + 2e^- \\
\text{HFeO}_2^- + \text{H}_2\text{O} &\leftrightarrow \text{Fe(OH)}_2 + \text{OH}^-.
\end{align*}
\]

Previous literatures also confirmed the usual presence of an additional oxidation peak (nearby-1 V vs. Hg/HgO) during the early Fe/Fe$^{(II)}$ conversion, which may be highly attributed to the oxidation of Fe to such soluble intermediates (see O$_2$ peak).\[63−65\] The following charge procedure (Fe$^{(II)}$-to-Fe$^{(III)}$ oxidation, see O$_1$ peak) quite differs from the original one due to the co-existence of multiple electrochemical pathways/intermediates. In this stage, FeOOH (metastable δ-FeOOH), Fe$_3$O$_4$, and Fe$_2$O$_3$ (the three most stable phases of Fe-VI group substances) are all conceived as the final products after deep charge reactions.\[65\] When discharging, the anode exhibits two main reduction peaks located at −1.05 V (R$_{II}$) and −1.16 V (R$_{I}$), which are indexed to reversible reactions of Fe$^{(III)}$-to-Fe$^{(II)}$ and Fe$^{(II)}$-to-Fe reductions, respectively. Thereafter, there is an intense/steepest cathodic current increase starting from −1.24 V and persisting upon deep reduction, corresponding to the hydrogen evolution reaction (HER) in alkaline electrolytes. The presence of HER phenomenon indicates that electrochemical standard potentials for hydrogen evolution and Fe(OH)$_2$/Fe reduction are very close, and the over-potential of H$_2$ evolution on Fe surface is quite low.

Fully understanding charge transfer reactions at the interfaces of electrode-electrolyte plays a key role in elaborating detailed charge storage mechanisms of ferruginous anodes.\[61,66,67\] In 2017, Weinrich and Balke have gained insights into Fe surface reaction processes in concentrated alkaline media using the powerful in-situ electrochemical atomic force microscopy, with an aim to establish real-time correlations between electrode topological changes and oxidation/reduction cycles at the nanoscale.\[61\] They put forward a typical model for the...
evolution of potentiodynamic redox layers on Fe surfaces, as schematically illustrated in Figure 2B-E. At the early stage of electrochemical reactions, FeOx passivation layers would be in-situ generated and cover on all electrode regions (Figure 2B) when Fe phases are exposed in alkaline electrolytes. During the first reduction process, such native FeOx layers gradually disappear (mostly through Fe₂O₃ or Fe₃O₄ dissolution followed by Fe(OH)₂ or nonstoichiometric hydrated substances precipitation), and the inner metallic Fe is uncovered for subsequent electrochemical reactions. Next, the metallic Fe as well as these evolved substances would become oxidized during the following anodic half cycle (Figure 2C), corresponding to reactions including partial Fe/Fe(OH)₂ dissolution and further oxidation into FeOOH. As a result, the original hydrated Fe⁴⁺ oxide species (e.g., HFeO₂⁻) significantly increase in amount, and moreover there reforms a thin/homogeneous passivation layer. This procedure proceeds in parallel to the oxidation of Fe electrode together with the precipitated particles. Note that this passivation of metallic Fe electrode is not irreversible; the electrode would be depassivated (at least partially) after a repeated reduction process (Figure 2D). Similar to the initial reduction procedure, the depassivation might proceed by the passivation layer dissolution and Fe(OH)₂ precipitation on existing particles for continuous growth. The repeated exposure of Fe to the alkaline electrolyte allows an additional redox cycle and enables a charge/discharge loop vividly described in Figure 2D,E. The precipitated particles would keep growing on Fe electrode considering the particulate size/amount in each cycle, but not necessarily form a dense layer as a barrier for the further oxidation of metallic Fe beneath. The accumulation of such discharge products may influence the electrode electrochemical reactivity, for example, by contributing more available amount of electrochemical actives, as confirmed by the capacity-rise phenomenon in early electrode activation steps.

When it comes to full-cell devices, the most investigated aqueous EES systems using iron-based anodes are nickel–iron (Ni–Fe) alkaline batteries [68–71]. Since invented by Waldemar Jungner and further patented/commercialized by Thomas Edison in 1897–1902, early Ni–Fe batteries had been used in stationary and mobile energy storage applications for over 70 years in United States and Europe. [68] The half-cell reaction at the cathode region is the reversible redox chemistry between nickel oxide-hydroxide (NiOOH) and nickel oxide (NiO); whereas, at the anode side, only a typical redox conversion of Fe/Fe⁴⁺ is involved (two-electron transfer), considering the long-lasting cyclic stability/endurance requirements for commercial usage. All related half/full-cell reactions are listed as follows [47]:

Cathode: 2NiOOH + 2H₂O + 2e⁻ ⇄ 2Ni(OH)₂ + 2OH⁻
(E⁰ = −0.88 V vs. Hg/HgO),
Anode: Fe + 2OH⁻ ⇄ Fe(OH)₂ + 2e⁻
(E⁰ = +0.49 V vs. Hg/HgO),
Full cell: 2NiOOH + Fe + 2H₂O ⇄ 2Ni(OH)₂ + Fe(OH)₂
(Ecell = 1.37 V).

After being precharged/discharged 20–50 times to achieve a stable capacity (called “battery formation” in cell industries), traditional Ni–Fe alkaline batteries can generally provide an open-circuit voltage of ~1.4 V and a stable output voltage of ~1.2 V in practical applications. There is a highlight that their cyclic stability can reach to 3000 cycles (calendar lifetime: ~20 years) even under the abusive usage such as mechanical shocks and vibrations. [68] Additionally, they are free of hazardous heavy-metal elements (like cadmium, lead, etc.) and cost-effective, principally suitable for various application situations. However, it is unfortunate that the partial utilization of ferruginous actives (the end oxidation product is Fe(OH)₂ rather than Fe⁴⁺-based species) limits the specific energy density and power density to only ~19-25 Wh kg⁻¹ and ~0.1 kW kg⁻¹, respectively. These values are lower than those of nickel–cadmium (Ni–Cd; 1.2 V, 40–60 Wh kg⁻¹, 0.15 kW kg⁻¹), nickel–zinc (Ni–Zn; 1.6 V, 100 Wh kg⁻¹, >3 kW kg⁻¹) and nickel-metal hydride (Ni–MH; 1.2 V, 60–120 Wh kg⁻¹, 0.25–1 kW kg⁻¹) batteries. [68] As a result, the early developed Ni–Fe batteries were rapidly replaced by sealed lead-acid cells (2.1 V, 30–40 Wh kg⁻¹, 0.18 kW kg⁻¹) after year 1980, the robust competitor with larger specific energy and power, maintenance-free property, better rate capability and even lower cost. To maximize the competitiveness of Ni–Fe batteries, making full use of ferruginous anodes via three-electron transfer proves an applicable way; such developed Ni–Fe alkaline batteries have been extensively studied in recent years. [47] During the deep discharge process of these advanced Ni–Fe batteries, a further anodic redox reaction proceeds:

Full cell: NiOOH + Fe(OH)₂ ⇄ Ni(OH)₂ + FeOOH
(Ecell = 1.05 V).

Note that the metastable FeOOH would gradually convert into thermodynamically stable Fe₂O₄ during the subsequent cycles (If aided by the addition of LiOH, Fe(OH)₂ can straightforward transform into Fe₂O₄ and thereby avoid the phase transitions [38,71]).

Although considerations of other analogous elements with multielectron redox behaviors have been
raised to design aqueous EES devices, most of them have not been commercialized yet. Unlike for either consumable electronics or electric transportation where the cell energy density is concerned primarily, the minimum price per kWh over its overall cycle lifespan (n-$/(kWh)^{-1}$, where $n$ is the total cyclic period) and the battery safety, are more critical concerns for grid-scale/sustainable stationary energy storage.\[72\] Figure 2F shows a comparison table listing key characteristics of Fe, Zn, and Mn transition metals as potential anodes in alkaline devices, and a radar plot with a scoring criterion (0–100) from the “inferior” to “superior” grade. By comparing with Zn and Mn, Fe holds great potential due to the following aspects.\[62\] Primarily, Fe is the most abundant transition metal resource (~47,000 ppm) in Earth’s crust and has the lowest price (~60–70 $/ton^{-1}$) among the three metal anodes, which means that Ni–Fe alkaline batteries would be more competitive in terms of resource cost.\[73\] Besides, Fe possesses attractive electrochemical features; its redox potential (~0.44 V vs. SHE) is ~0.3 and ~0.74 V, higher than that of Zn and Mn anodes, respectively; thus, the influence of H$_2$ evolution can be significantly reduced, beneficial to optimizing the cyclic stability.\[74\] By means of three-electron transfer, the elemental Fe would theoretically deliver a large specific capacity up to ~1441 mAh g$^{-1}$ and an impressive volumetric capacity of ~7558 mAh cm$^{-3}$\[75\] either of which is much greater than Zn anode, the major competitor of Fe.

In conventional aqueous alkaline batteries, despite that the paired cathode could be Co-based oxides or hydroxides,\[76–78\] the most promising cathode material is still NiOOH that is commercialized in Ni–MH batteries. As discussed above, iron-based anodes in these EES devices generally store energy based on conversion reactions, giving rise to a high specific capacity. Note that this charge-storage mechanism can be readily applied in hybrid EES devices, such as aqueous battery-supercapacitor hybrid devices consisting of one battery electrode and one capacitive electrode.\[77\] In addition to conversion mechanism, some iron-based anode materials like Fe$_2$O$_3$, Fe$_3$O$_4$, and FeS$_x$ have been demonstrated with highly pseudocapacitive behaviors in mild electrolytes for use in aqueous asymmetric supercapacitors. By setting within an appropriate potential window and using proper electrolytes, fast faradaic reactions nearby the surface region (rather than sluggish bulk conversion) can be ensured, which contributes to far more stored energy than that of typical electric double-layer capacitors.\[48,53–55,63–65\]

### 2.2 Innovative EES devices

#### 2.2.1 All-iron batteries

Advances in battery technology trigger the continual development of more innovative EES devices. Different from Ni–Fe alkaline batteries, many fresh concepts have been springing up. As a typical example, Zhao et al. recently proposed “all-Fe” secondary battery systems (the anode material, cathode material and electrolyte are all ferruginous species) by employing solid Fe/Fe$_3$O$_4$ and soluble ferricyanide as the anode and cathode materials, respectively (Figure 3A).\[79\] In this battery configuration, expensive solid cathodes (containing transition-metal elements of Ni, Co, Mn, etc.) are substituted by low-cost ferricyanides with faster reversible redox kinetics, exhibiting great potential as grid-scale EES devices in widespread power-supply implementation. During the charge/discharge operation, K$^+$ and OH$^-$ migrate through the Nafion membrane to form a complete electrochemical cell. Herein, the purpose of using Nafion separator is to prevent the adverse shuttling of ferricyanide ions (Fe(CN)$_6^{3-}$, Fe(CN)$_6^{4-}$), thereby reducing the undesired self-discharging and corrosion reactions. The anode reaction mechanism is totally identical to the case aforementioned in conventional alkaline Ni–Fe batteries, but at the cathode side the mechanism is based on electrochemical conversion between Fe(CN)$_6^{3-}$ and Fe(CN)$_6^{4-}$:

\[
\text{Cathode: Fe(CN)$_6^{3-}$ + e$^-$} \rightleftharpoons \text{Fe(CN)$_6^{4-}$} (E^0 = +0.36 V vs. SHE).
\]

The anode/cathode CV plots (Figure 3B) reveal the potential difference approaches 1.2 V, highly in line with the theoretical calculation. This voltage value is comparable to, or even overpasses that of classic rechargeable batteries such as alkaline Ni–MH, Ni–Cd, and Ni–Fe, or the acid polysulfide-I$_2$ cells, and so on.\[27,29,31\] Figure 3C presents the cost of active species of state-of-the-art aqueous batteries, including vanadium redox battery and other classic alkaline batteries by referring to the following “cost analysis” equation:\[79\]:

\[
C = \frac{3600}{EF} \sum_i Q_i M_i \frac{n_i}{n}
\]

where $C$, $Q$, and $M$ represent the cost per kilowatt-hour ($\$/kWh$^{-1}$), the cost in specific mass, the molecular mass for redox materials, while $E$, $F$, and $n$ are assigned to the cell voltage, Faraday’s constant and electrons number in redox reactions, respectively. The total raw
material cost of $22 \text{ kW h}^{-1}$ is only around one fifth of the value for all-vanadium batteries ($118 \text{ kW h}^{-1}$), and lower than polysulfide-I$_2$ ($86 \text{ kW h}^{-1}$) and commercialized Ni-Cd cells ($51 \text{ kW h}^{-1}$).\cite{81-83} Also note that such configured all-Fe batteries are free of dendritic growth issues, and thereby still competitive to Zn-Ni alkaline cells with nearly the same cost.\cite{79} In spite of merits in affordable active materials cost and operation stability, several tough challenges still stand in the way, mainly involving the high battery polarizability resistance (thus low operating power density), imperfect active homogeneity, small utilization ratio (30\%–40\%) in anodic species and the need for separator use. To boost the utilization efficiency and decrease the high ohmic resistance, much more attention should be paid to further systematic optimization of the key battery parameters (e.g., energy and power densities, cyclic stability, etc.) and constitutions.

Apart from the choice of conventional concentrated alkaline electrolytes, all-Fe batteries can also be constituted based on the acid or near-neutral electrolyte conditions. Actually, corresponding cell prototypes with quite low-cost, nonhazardous and highly reversible characteristics have been early proposed by Hruska and Gong et al. The aim of using a same active element of Fe to build two sets of redox reactions at both anode and cathode is to avoid undesired crossovers of redox species/derivatives (also named as “electrolyte contamination”
Fe²⁺ in most cases) can be released from the supplier, anode and a host cathode. During discharging, Fe²⁺ can be reversibility deinserted or dis-inserted from the host cathode into the electrolyte, and Fe metals. Anode: Fe⁰ ↔ Fe²⁺ + 2e⁻ (E⁰ = −0.44 V vs. SHE),
Full cell: 2Fe³⁺ + Fe⁰ ↔ 3Fe²⁺ (E cell = +1.21 V).

However, their further progress and commercialization are greatly impeded by either technical or economic barriers, including intense HER side reaction in acid conditions, using costly organic TEOA ligands to yield Fe ions-coordinating redox actives, or any other kinetic problems. Besides, such configured full battery devices (See testing data in the literature) seem more like primary cells that run based on the continual consumption of fresh Fe³⁺ salts (need ceaseless updating) and Fe metals.

2.2.2 | Rocking-chair Fe-ion battery

In addition to fundamental research on selecting novel iron-ion redox couples for EES device assembly, great efforts are also directed to rocking-chair battery systems relying on Fe²⁺ ions shuttling between Fe metal anodes and feasible host cathodes. This battery design is enlightened by acidic all-Fe cells and currently popular zinc (Zn) metal batteries, enabling more competitive in reactivity/dynamics, power and energy densities. Different from all-Fe batteries, the rocking-chair Fe-ion battery refers to a battery system composed of an iron supplier anode and a host cathode. During discharging, Fe-ions (Fe²⁺ in most cases) can be released from the supplier, and inserted into the host lattices or form insoluble species anchoring on the electrode surface. While during charging, Fe²⁺ can be reversibility deinserted or dissolved from the host cathode into the electrolyte, and return back to the supplier anode. The supplier electrode side, at least, needs to be Fe-based materials. By imitating zinc working mechanism, Ji’s groups have demonstrated that Fe metals hold a remarkable promise to compete with Zn anodes, since they can also undergo an analogous reversible Fe plating/stripping process in a FeSO₄ salt solution (pH value: ~3–5):

Fe⁰(S) ↔ Fe²⁺(aq) + 2e⁻ (E⁰ = −0.44 V vs. SHE).

Typical CV plot of Fe plating/stripping in a half-cell system (Figure 3D) shows the cathodic (Fe plating) current rises rapidly below a potential of −0.20 V (vs. Fe²⁺/Fe), with a relatively high over-potential to overcome energy barriers of Fe²⁺ dehydration, and Fe absorption/nucleation; whereas, the reverse Fe²⁺ stripping process gives rise to a lower over-potential of ~50 mV due to the faster Fe/Fe²⁺ reaction kinetics. Galvanostatic charge/discharge (GCD) profiles of as-built Fe||Fe cells (inset in Figure 3D) display very little potential polarization variations (from ~0.23 to ~0.28 V) are observed after 500 times of repetitive Fe plating/stripping processes (500 h; without battery short-circuit), demonstrating their excellent operation stability. Though the overall polarization is ~0.25 V (~0.17 V higher than Zn case in ZnSO₄ electrolytes), the dendrite-free property (confirmed by SEM observation toward plated Fe; Figure 3E) makes Fe anodes very stable and safe in symmetrical Fe||Fe cells testing. However, configuring such batteries with Fe²⁺ as an ionic charge carrier for reversible topotactic (de)insertion is difficult due to the following strict cathode selection criteria. The electrolytic Fe²⁺ ions are never allowed to oxidize into Fe³⁺ at the redox potential of working cathodes since chains of side reactions (comprising the Fe³⁺ hydrolysis and subsequent Fe(OH)₃ precipitation, etc.) would follow. Another pivotal consideration is the cathode manufacturing cost. It should be, at least, comparative to that of inexpensive Fe anodes; otherwise, constructing Fe-ion batteries would become meaningless because they are uncompetitive with traditional aqueous batteries on energy/power densities or long cyclic endurance. In a survey exploration of cathode candidates, V₂O₅, LiFePO₄, FePO₄, ferricyanide (like K₄Fe(CN)₆), MnO₂ and Prussian blue analogues are potentially redox couples. Fe³⁺[Fe²⁺(CN)₆]₀.₇₅·3.₅H₂O (IPB), a type of insoluble Prussian blue analogue with robust framework architecture and proper redox potential is a good cathode choice. The constituted full-cell system (Figure 3F; comprising Fe anode, IPB cathode and FeSO₄ electrolyte) shows a low over-potential of ~0.23 V, and this value could be further reduced under a higher Fe²⁺ concentration condition.

Compared to cathodes made of rare, high-price or renewable elemental resources, the cost-effective and earth-abundant S is unquestionably the most promising electrode material for scalable development of sustainable...
battery technologies.\textsuperscript{[101–104]} In impressions, the practical use of S cathode is exemplified by the mature commercialization of high-temperature Na–S cells, and near-industrial room-temperature Li–S cells.\textsuperscript{[105–110]} Except for Li, Na, or K, the alkaline-earth metals and other candidates (denoted as x) are also studied to couple with S (see the diagram in Figure 3G).\textsuperscript{[106]} However, such metal–S cells have to run in nonaqueous electrolytes, and confront issues led by intermediate polysulfides dissolution and accompanied shuttling effects, causing severe active losses, limited cyclic lifetime, and inferior Coulombic efficiency. The addition of metal chalcogenides into cell systems may restrain the polysulfide shuttling due to the creation of metal–S bonding, or metal sulfide minerals that differ from LiS\textsubscript{n}/NaS\textsubscript{n} and keep stable in organic solvents.\textsuperscript{[108,111–113]} Enlightened by reversible Fe\textsuperscript{2+} rocking-chair reacting behaviors, Wu et al. creatively achieved a fresh aqueous battery system that combines Fe metal anode and S cathode. This battery chemistry is of tremendous interest because S actives and all discharging intermediates are immobilized; the setup is totally free of polysulfides dissolution and shuttle phenomena due to the extremely low solubility for either S (\(-1.5 \times 10^{-7}\text{M}\)) or FeS\textsubscript{n} (\(-2.31 \times 10^{-22}–2.21 \times 10^{-7}\text{M}\)) in aqueous solutions.\textsuperscript{[80]} Figure 3H–I show the basic battery configuration, working principle and redox mechanism, with a stepwise all-solid-state phase conversion (S\textsubscript{8} \leftrightarrow FeS\textsubscript{2} \leftrightarrow Fe\textsubscript{3}S\textsubscript{4} \leftrightarrow FeS) and a low volume expansion ratio (\(-32.6\%\)). The battery discharging entails Fe\textsuperscript{2+} ions stripped from Fe anode, and meantime the S cathode would take in Fe\textsuperscript{2+} to form FeS\textsubscript{n} initially, delivering a high specific capacity of \(-1050\text{mAH g}^{-1}\). Note that this process totally differs from the case for Li/Na–S cells; the Fe\textsuperscript{2+}-storage mechanism in S is unique and more influenced by physical conditions of cathodes (e.g., available pore volume, ionic access channels, etc.), rather than the often concerned S loading ratio.

Besides nonmetal S (or extended chalcogenes like Se and Te) cathodes, the elemental iodine (I\textsubscript{2}) may also trigger great scientific enthusiasm in aqueous EES devices due to its abundance in ocean and eco-friendly nature, quick I\textsubscript{2}/I\textsuperscript{-} reaction kinetics and considerable theoretical specific capacity (\(-211 \text{mAH g}^{-1}\)).\textsuperscript{[114–116]} However, some tough obstacles, including adverse I\textsubscript{2} disproportion/parasitic reactions in either alkaline or acidic aqueous solutions, and undesired shuttling effect of iodine species, still require addressing carefully.\textsuperscript{[117]} These factors would deteriorate the capacity retention and other operation parameters, or even cause a sudden battery failure. Recently, Yuan et al. have achieved a rechargeable Fe–I\textsubscript{2} battery system wherein Fe anodes are purposely modified with ascorbic acid.\textsuperscript{[118]} Moreover, the use of N-doped carbon scaffolds can suppress the ceaseless shuttling of I-related species. Such configured batteries exhibit high specific capacity/energy (Max.: \(-190\text{mAH g}^{-1}; 130\text{Wh kg}^{-1}\) at 356 W kg\textsuperscript{-1}), salient power density (\(-1300\text{W kg}^{-1}\) at 120 Wh kg\textsuperscript{-1}) and good cyclic stability, capable of coupling directly with solar cells.

In spite of former advances in Fe-ion batteries, Fe anodes in the absence of any protective modifications have to be subjected to undesired side reactions (e.g., HER, serious metal passivation, etc.) in acid aqueous electrolytes, hence leading to unsatisfied Coulombic efficiency (CE; average value: \(-90.7\%\)) among repetitive charge/discharge processes. More future works deserve focusing on how to suppress or eliminate such side reactions.

### 2.2.3 | Multifunctional “battolyser” device

Green EES devices (like less-toxic iron-based batteries/ supercapacitors aforementioned) and clean fuels (H\textsubscript{2}, NH\textsubscript{3}, CH\textsubscript{3}OH, etc.) are both crucial to the development of future sustainable society.\textsuperscript{[119–121]} However, the mass fabrication of these artificial fuels usually needs beginning from the basic N\textsubscript{2}, H\textsubscript{2}O, and CO\textsubscript{2} resources and ending with the vast generation of exhaust emissions, which is not environmentally friendly for practical utilization. Also, the fuels synthesis (like H\textsubscript{2} made by water splitting) and electricity storage are independent, both requiring durable battery and efficient electrolyser assistance. To maximize the electrochemical conversion efficiency, Mulder et al. have reported a “two birds with one stone” methodology by combining Ni–Fe alkaline cells and H\textsubscript{2} production into an integrated battery-electrolyzer (short for “battolyser”; Figure 4A), where the electricity is efficiently stored into batteries and meantime the water splits into gases.\textsuperscript{[112]} The working mechanism is listed below. During the full charge process, NiOOH and Fe\textsuperscript{0} nanostructures evolved successively from Ni(OH)\textsubscript{2} and Fe(OH)\textsubscript{2} electrodes would function as efficient catalysts for HER and O\textsubscript{2} evolution reaction (OER). From the perspective of energy conversion, the charged electrodes use the all redundant electricity to drive H\textsubscript{2}O electrolysis, exhibiting a remarkable energy efficiency up to 90\% (far overpassing the Max. energy utilization efficiency of 70\% for individual Ni–Fe batteries, and \(-70\%\) for alkaline electrolyser; bottom in Figure 4A). This simultaneously increases actives utilization ratio by 50\% (the optimized energy density reaches the highest 250 Wh L\textsuperscript{-1}) and protects the battery overcharge.\textsuperscript{[112]} Figure 4B shows the battolyser functionality and possible application areas. The image in left side refers to such a layout of integrated
Electrochemical battery and electrolyser devices. The charge of Ni–Fe cells enables the electricity (coming from intermittent/renewable energies) stored into electrode materials by redox conversion reactions; once fully charged, H2 and O2 begin to yield via H2O electrolysis based on the following equations:

Cathode: \( 4\text{OH}^{-} \xrightarrow{\text{Overcharge}} \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \),
Anode: \( 2\text{H}_2\text{O} + 2\text{e}^- \xrightarrow{\text{Overcharge}} \text{H}_2 + 2\text{OH}^- \).

The in-between diaphragm is responsible for ionic commuting of \( \text{OH}^- \) and segregation of above two gases. Such “two-in-one” devices may be used to supply electricity and H2 fuel for plug-in hybrid electric and hydrogen vehicles, stabilize the electricity grid and work for H2 feedstock as well.[122]

Figure 4C shows the battolyser charge utilization in the electricity storage and H2 production divided by a cell device with a nominal capacity of 10 Ah. Interestingly, the H2 evolution launches immediately even at small current rates and almost among the entire charge stage, quite different from the OER case. This may be readily understood since nearly no NiOOH remained to start the O2 production (but some Fe residues still exist and support the HER) after the full discharge stage. Further, Bernhard et al. have newly put
forward the hybrid concept of “H2/electrical energy storage” by upgrading cell systems (Figure 4D); multiple Ni and Fe-based electrodes with respective functions are simultaneously configured (rather than using a single anode or cathode), thereby well permitting the decoupling of electrode usage for both battery operation and H2 evolution. The incorporation of a H2 storage or delayed generation strategy, and a novel control style for energy-storage cells would allow for current control/distribution at distinct electrode regions with specific purposes. This device configuration may be quite useful and applicable when the electricity is cheap and rich at overnight time slots; a fraction of electricity turns into H2 resources, while the other can be stored into grid-scale power stations for electricity compensation/peak-power supply.

3 | FAILURE MECHANISM AND DESIGN STRATEGIES

3.1 | General failure mechanism of iron-based anodes

Every coin has two sides. Despite the remarkable redox behaviors of iron anodes in various aqueous EES devices, there are still several formidable challenges that need to be addressed, such as unstable cyclic stability, poor capacity utilization, limited rate capability, and notable self-discharge rate. These issues are not only caused by undesirable HER from water in the electrolyte, but also strongly correlated with the specific charge storage mechanisms discussed in the former sections, which probably result in charge-transfer limitations, bulky volume expansion, inevitable structural dissolution/reconstruction and gradual inactivation/passivation by nonreducible surface oxide films. To break these major technical bottlenecks, intrinsic fatigue/failure mechanisms need to be profoundly unveiled by gaining a fundamental understanding toward phase changes during iron-anode operation.

As early as 1976, Ojefors et al. tried to collect the evidence to confirm the dissolution-precipitation discharge process of iron anodes by means of SEM observations. Unfortunately, more in-depth insights into electrochemically induced crystalline variations on iron anode can hardly be acquired due to the lack of powerful and real-time characterization techniques. Recently, Yushin et al. have subdivided the evolution of iron anodes in alkaline electrolyte into four distinct stages, nominally comprising “development (Stage I), retention (Stage II), fading (Stage III), and failure (Stage IV)” (Figure 5A) during

![Figure 5](https://example.com/figure5.png)

**Figure 5** (A) A schematic describing the evolution of Fe anode into four distinct stages: “development (Stage I), retention (Stage II), fading (Stage III), and failure (Stage IV). (B) The typical cyclic performance for Fe metal anodes, and (C) XRD monitoring on their phase changes during cycling. Reproduced with permission. Copyright 2018, American Chemical Society
the total cycling period (Figure 5B), which was aided by the postmortem analysis such as X-ray powder diffraction (XRD) monitoring (Figure 5C) toward Fe actives in a broader potential window. Each stage is correlated with a specific dynamic change on the electrode morphology and structural phase. The CV testing in this study reveals that both the discharge capacity and Coulombic efficiency of Fe anodes gradually increase during the initial 50 cycles and achieve the maximum, maintain almost constant within later 50–80 cycles, undergo the rapid decay to their minimum at the 120th cycle, and then retain the small values till the end of cycling. XRD analysis uncovers that the metallic anode is highly reversible and dominant in component, in the absence of notable electrically/electrochemically isolated oxides within Stage I. In subsequent Stage II, little changes in either electrode surface or electrochemical behaviors are observed. However, XRD patterns clearly reveal an increasing signal arising from maghemite (γ-Fe₂O₃, a cation-deficient form of Fe₃O₄; with the same crystal structure/space group to Fe₃O₄ when cation vacancies are randomly distributed over octahedral interstitial sites). In parallel, with further anode evolution, ex-situ SEM observations also disclose the onset formation of octahedral γ-Fe₂O₃ products, and more significantly the presence of basalt-like Fe fragments caused by “dissolution-precipitation” processes of intermediate actives. At Stage III, the accelerated anode degradation is highly ascribed to the accumulation and aggregation of such isolating and low-reactivity γ-Fe₂O₃ crystals (electronic conductivity: 1.8 × 10⁻⁸ S cm⁻¹, much lower than that of magnetite at room temperature: 250 S cm⁻¹). This fundamental research work suggests that the effective prevention of irreversible nucleation and growth of γ-Fe₂O₃ phase may play a crucial and essential role in minimizing the capacity fading of ferruginous anodes in aqueous EES devices.

As for the acidic or near-neutral electrolyte conditions, the failure of ferruginous anodes is governed by acid etching that obeys the general Fe corrosion mechanism. Taking the most utilized Fe metal anode as example, the anode tends to be etched by H⁺ to form Fe⁺⁺ species, and then further oxidized into insoluble Fe⁺⁺⁺ substances (like FeOOH) when exposed in electrolytes. Worse still, this corrosion process would be accelerated by the presence of HER on Fe anodes during battery operation. Though compact passivation layers can be formed on anode/electrolyte interfaces to protect the electrode from the corrosion, the as-built thick passivation films would in turn block the ions diffusion, eventually deteriorating the redox reaction kinetics and thus expediting the anode failure.

3.2 | Key strategies to optimize iron-based anodes

3.2.1 | Suppression of HER

In general, besides the basic redox reactions of ferruginous materials, there are side reactions involved at the anode side. The most common one is HER, which not only influences the stability of anode (Fe metal could be thermodynamically unstable and prone to suffer from severe electrochemical corrosions once the HER proceeds), but also may lead to safety concerns in practical applications. Although adopting a narrower operation potential window may avoid excessive phase-transition reactions, a remarkable capacity loss would come along as well. As another alternative choice, literatures confirm that the addition of sulfide salts (e.g., Na₂S, FeS, and Bi₂S₃), elemental sulfur or organo-sulfur molecules, either to the solid electrode or to the alkaline electrolytic solution, can greatly suppress the HER phenomenon and optimize the iron-based anodes. For instance, Marcus et al. compared the first galvanostatic discharge curves of ferruginous anodes in the alkaline electrolyte without and with 0.01 M Na₂S additive (Figure 6A).

The significant positive effect of sulfide additives is clearly confirmed, as the pronounced H₂ evolution is evidently suppressed, and an increased discharge capacity (maximum value: ~1.43 μAh cm⁻², surpassing the level of ~1.1 μAh cm⁻² without additives) can be observed in Na₂S-contained alkaline electrolytes.

To account for the detailed inhibition mechanism of Na₂S on ferruginous anode, the X-ray photoelectron spectroscopy (XPS), and especially time-of-flight secondary ion mass spectrometry (ToF-SIMS) were employed. For ToF-SIMS, the variation of ionic intensities with sputtering time may to some extent reflect the significant in-depth concentration information. Figure 6B shows ToF-SIMS negative ions depth profiles of the cycled samples with 0.01 M Na₂S additive (Fe²⁻, FeO⁻, 3⁴S⁻ and NaO⁻/KO⁻ ion depth profiles are successively recorded to characterize the Fe metal, FeOₓ/Fe(OH)ₓ and distinct electrolytic species). The maximum intensity of 3⁴S⁻ ions profile between 500 and 1030 s sputtering confirms the S-contained substances adsorption/accumulation at the interfacial region between the Fe substrate and oxide layer, rather than on the top electrode surface. As discussed, such adsorbed S species could generate chemical bonds with metallic Fe so as to weaken bonds between Fe atoms
and their adjacent neighbors in the metallic subsurface interface, and accelerate Fe dissolution to yield a thicker FeOx/Fe(OH)ₓ film for HER inhibition. It is interesting to note that the as-formed thicker oxide film is made up of numerous columnar submicro units, with observable porous structures that are more obvious near surface zones and may disappear nearby the substrate interface. The working mechanism of Na₂S additive in suppressing HER has been depicted by the authors. A thin native oxide layer initially existing on pristine Fe anode surfaces is electrochemically reduced, and then the exterior surface of Fe becomes irregular and rough, which thus benefits for the later S adsorption. Principally, S ads in electrolyte media would accumulate at the Fe/oxide interface (preferentially at defective sites) and help to suppress the HER. These adsorbed S ads facilitates the Fe anodic oxidation, resulting in the formation of thick but porous FeOₓ/Fe(OH)ₓ columnar film (See the inset in Figure 6B). The porosity nature of as-formed ferruginous oxide layers can support the reversible redox (de)conversion reaction of Fe(II)/Fe(III) among the subsequent charge/discharge processes.

As for the acidic electrolyte situations, the addition of S-based substances would become impracticable due to the quick hydrolysis reactions of sulfide salts in H⁺-rich aqueous solutions. To minimize the HER effects and improve the performance of Fe metal-based cells, ameliorating the electrolyte conditions by bringing in extra additives would be a feasible way. Very recently, our groups have proposed to suppress the HER of Fe anodes, and meanwhile elevate their kinetics with NH₄Cl regulator, a historical chemical agent used as the additive agent in Zn–Mn primary batteries. Figure 6C schematically shows the basic working principles for battery systems made of Fe metal foams, nano carbon foams, and NH₄Cl-involved FeSO₄ electrolyte. The NH₄Cl additives plays a “buffering agent” role in raising the electrolyte pH value forward the neutral direction; thereby, the electrolyte with less H⁺ concentration would not incur the formation of thick and dense inert films covering on Fe metals and blocking Fe²⁺ diffusion. Adding NH₄Cl would increase the ionic conductivity of electrolyte; also, the electrolytic salt would help to etch the dense and compact passivation layers covering on Fe metals, remarkably boosting the reaction kinetics of anodes (e.g.,
more expedite Fe plating/stripping, quick Fe$^{2+}$ shuttling, far lower anode polarization, etc.). As verified by CV plots in Figure 6D, the CV profile in NH$_4$Cl/FeSO$_4$ electrolyte definitely shows the smallest peak separation and strongest peak current signals when compared to using other electrolytes (e.g., in either FeSO$_4$, FeCl$_2$, or multicomponent FeSO$_4$/NaCl, FeSO$_4$/KCl mixture solutions). Note that this battery system is distinct from conventional flow-type EES devices aided by the use of ion-exchange membranes. Extra yellow solid products of $(\text{H}_2\text{O})\text{Fe}_2(\text{SO}_4)_2(\text{OH})_6$ would form on the cathode side when cells are fully charged, but then disappear in later discharging process.

### 3.3 Hybridization designs

In some cases, iron compounds, especially various iron oxides, were used as the anodes in aqueous EES devices. Except for the magnetite Fe$_3$O$_4$, it is unfortunate that nearly other FeO$_x$ are all wide-band semiconductors or even close to insulators (e.g., electronic conductivity of Fe$_2$O$_3$: $\approx 10^{-14}$ S cm$^{-1}$). Consequently, the electrode kinetics affected by poor electrons transport, particularly at high charge/discharge rates, would restrict the total utilization ratio of active materials and greatly reduce the capacity and energy density. In addition, the anodic conversion reaction leads to significant volume changes and newly formed less conductive species; the structural instability and electron transport limitations in iron oxide anodes are then presented simultaneously and thereby more challenging. To address these intrinsic issues, there have been continuous efforts devoted to optimizing ferruginous anodes in the past decades, mostly via a universal and very popular concept of “hybridization.” We have to admit that the combination of iron oxide anode with carbonaceous materials (graphene, carbon fibers/nanotubes, graphitic, or amorphous carbons, etc.), an “old trick” in chemical science and engineering for strengthening specific properties of material systems or remedying their performance drawbacks, is indeed the most effective and preferable way to build advanced functionalized hybrid iron-based anodes.[73-76] Numerous hybrid examples consisting of nanosized ferruginous anodes and diverse carbon species were reported in literatures.[140-154] Since there are already reviews or focused articles elsewhere on this subject,[38,53-55] we would thereby not purposely elaborate this part for readers. Though hybridizing with carbon plays a crucial role in alleviating electrode structural changes and improving the electronic conductivity, the capacity fading tendency for packed cells is still existing. Aimed to achieve better cyclic performance, cautious optimization of carbonization temperature and precursor concentrations is indispensable since these technical parameters are linked directly to carbon crystallinity, defects, thickness/permeability, wettability and porous nature, and thus highly associated with the ultimate electrochemical attributes. It was found that a thin conformal carbon layer (<6 nm) is not robust enough to restrain the volume expansions, while a too thick one (>25 nm) would impede ions diffusion into inner deep regions, and also cut down the weight percent of iron-based actives in anode.[143,148] Also, once the high carbonization temperature is utilized to guarantee the electronic conductivity of whole electrode, the as-formed graphitic carbon layers adhering to iron oxide surfaces are probably negative for ionic penetration, and hence restrict the inner redox reactions.

Unlike most iron oxides, the elemental Fe may have great potential in serving as the working anodes, since the metal itself own superior physicochemical properties (e.g., excellent electronic conductivity, remarkable theoretical capacity). Nevertheless, the downsized iron anodes typically have undesired ultrahigh electrocatalytic activity and inferior chemical stability, and thus they need to be hybridized, or fully packaged/encapsulated with graphitic carbon. The early typical example is trapping metallic Fe nanoparticles into self-adapting carbon nanoreactors (Figure 7A).[73] Particularly note the developed in situ evolution method enables the formation of single-phased Fe nanoparticle cores (mean size: ~60 nm; inset TEM), without yielding Fe$_3$C by-products that can irreversibly react with aqueous electrolytes. For the anode of Fe@C hybrids, the conformal construction of well-crystallized carbon shells are confirmed beneficial to stabilize the anodic performances in alkaline electrolytes and meanwhile prevent irreversible side reactions in effect. Lately, Wu et al. reported a unique and scalable way to produce high-performance hybrid anodes based on active Fe nanoparticles conformally sealed within carbon shells.[75] Interestingly, by means of the aerosol-assisted pyrolysis technique (Figure 7B), air-stable Fe nanoparticles can be obtained, attributing to the in situ formed Na$_2$CO$_3$ protective layers on Fe. The core-shell C-Fe anodes (inset TEM) demonstrate high electrochemical activity and stability, with a high specific capacity and a great capacity retention ratio of 93% even after 2000 cycles.

Generally, iron-based hybrid anode materials are used in powder forms; with that, carbon black and polymer binder additives have to be involved when fabricating the electrode. The use of electrochemically inactive species not only hinders the charge/ion transport within the electrode, but also reduces both gravimetric and volumetric energy densities of the EES devices.
This kind of slurry electrode is not so bendable/flexible for specific applications. The alternative use of 3D anodes grown directly on conductive current collectors would not only simplify the electrode manufacturing and save the extra electrode additives, but also provide unique advantages including direct electron transport along specific direction, shortened ions diffusion pathways, more sufficient electrode-electrolyte contacting areas, and proper mechanical accommodation/release for strains induced by anodic phase transformation.[63,64,114,143,149,150] A recent typical example is the use of conformal surface coating strategy to design hybrid arrayed Fe3O4 nanorods via atomic layer deposition (ALD) technique.[150] The resultant Fe3O4@TiO2 core–shell nanorod arrays demonstrate the following inherent advantages (Figure 7C): (i) ALD technique ensures high uniformity and precise thickness control of TiO2 shells, and their robust mechanical adhesion to Fe3O4; (ii) the outer TiO2 is a classic Li+ intercalation anode with less volume change, capable of acting as a durable “armor” against volume expansion of inner Fe3O4 nanorods during charging/discharging; (iii) the presence of TiO2 shells contributes to additional capacity via Li+ surface adsorption/desorption, and also partially suppresses the HER; (iv) straightforward alignment of individual nanorods onto current collectors enables direct electrons transfer and easy electrolytic penetration into entire electrode regions. Consequently, such integrated products show exceptional cyclic behavior over 30,000 times among a wide potential window in a neutral lithium salt electrolyte. Nevertheless, the poor electrical conductivity of TiO2 is not beneficial to guarantee the rate performance of the anode. The mixed combination of conducting carbon and semi-rigid oxide layers would be an efficient way to settle the above challenging issue. Lately, a homogenous mixed MoO2–carbon nano layer coating on magnetite nanorod arrays has been built to consolidate both the cyclic stability and reversible capacity of Fe3O4 anode for fully binder-free Ni–Fe alkaline batteries.[143] The reason for alternative use of MoO2 is given its robust ability to resist inner stress variations, additional capacity contribution via surface ions (Na+, K+) adsorption/desorption, and particularly the amazing metallic conductivity over 10^4 S cm⁻¹.

In addition, combining the advantages of Fe and other elements (Mn, Zn, Bi, Ti, etc.) may be a promising strategy to build better iron-based aqueous EES devices (Figure 7D).[46,48–50,59] A recent demonstration is the
incorporation of Fe into bismuthic anode systems to form ternary BiFeO$_3$ materials.$^{[46]}$ As a consequence, the desired electrochemical properties of Bi and Fe-based electrode actives would be perfectly integrated into one functionalized system. Note that this is a mutual “merits combination/complementation” strategy. The introduction of foreign Bi atoms into ferruginous oxides can evidently promote the overall electronic conductivity of anodes, and meanwhile restrain the ferruginous catalysis. Reversely, strong electrovalent interactions bridged between Fe and Bi (in BiFeO$_x$) would in turn elevate the fusing temperature of bismuthic products from ~271 up to 500$^\circ$C beyond, allowing them being encapsulated by carbon matrix via high/medium temperature treatments.

4 | FUNCTIONALIZATION OF IRON-BASED AQUEOUS EES DEVICES

Iron-based aqueous EES devices are promising for large-scale energy storage applications. They are, however, probably functionalized for use in future emerging fields. The rise of modern wearable technologies used in fields of sports, healthcare, the Internet of Things, smart robotics, defense and maintenance would empower a paradigm shift from traditional energy/power-oriented cell systems to specially functionalized (e.g., second-skin-like, ultralightweight, soft, flexible, wearable) power sources.$^{[155–157]}$

This is an imperative trend for iron-based EES systems as well. Primary concerns for development of these devices are to ensure their good comfortability of wearing experience, pretty high security together with preeminent mechanical durability and strength. These EES devices should require close attachment between actives and current collectors all the time, which is a fundamental prerequisite for flexible applications. However, traditional electrode actives and additives are in the powder forms, bringing challenges in keeping active materials well-adhered onto current collectors when full-cell devices suffer from numerous times of bending. Therefore, how to realize the electrode flexibility plays a decisive role in constructing smart functionalized power-supply devices. In general, flexible electrodes are fabricated using two main strategies.$^{[155]}$ One approach is directly coating/depositing electrode materials (by mixing redox actives with a significant amount of polymer binders and conducting additives) onto soft skeletal frameworks (like textile fabrics), or in-situ growth of electrochemical actives with abundant active centers on thin metal foils to eliminate any conductive agents and binders. The other is to redesign devices at the microscale, typically enlightened from the perspective of bionics and paper-cutting art.

Among various functional EES devices, fiber-shaped rechargeable (FAR) batteries are regarded as a potential category of fabric-like energy-storage devices for miniaturized, portable and wearable electronics due to their intrinsic merits of lightweight, super-flexibility, great compactness, and effort-less weavability.$^{[157–160]}$ They are more preferable to power wearable devices when compared to fibrous supercapacitors with remarkable power density and cyclic lifespan but quite limited specific energy and unstable output voltage. Construction of Fe-based FAR aqueous alkaline batteries requires cathode materials of Ni, Co, Mn, and V-based oxides/hydroxides, sulfides and phosphides. They can provide sufficient specific energy and safety for our daily usage (Figure 8A). One early example was reported by Xiao et al. via a defect engineering-based superficially doping strategy to make FAR alkaline Ni/Fe batteries.$^{[159]}$ Defect-rich shells are yielded on surfaces of NiO and Fe$_2$O$_3$ nanostructures grown on Cu fibers, which effectively boosts the capacity, rate performance and durability of electrodes (see battery configurations in Figure 8B). According to calculation analysis on the density of state for pure or Mn-doped Fe$_2$O$_3$ crystals, the Fermi level crosses the electron states after one Mn atom doping into original Fe$_2$O$_3$ cells, which suggests a narrower bandgap energy and improved carrier density for electron transport (Figure 8C). The assembled FAR alkaline Ni/Fe batteries with gelled electrolyte delivers remarkable volumetric energy density of 61.0 mWh cm$^{-3}$ and power density of 48.4 W cm$^{-3}$, 91.2% capacity retention after 30,000 cycles, and excellent mechanical stability under varied testing conditions (bending angle range: 0°–180°, compressed weight: 100 g; Figure 8D). More recently, Yao et al. proposed the assembly of all-solid-state NiCo/Fe FAR alkaline batteries made of free-standing core-shell NiCoP@NiCoP nanoflake arrays (cathode) and TiN@Fe$_2$O$_3$ nanowire arrays (anode), both of which are firmly grown on carbon nanotube fibers for wearable utilization concerns.$^{[158,160]}$ The choice of transition bimetallic phosphides as high-capacity working cathodes (1.07 mAh cm$^{-2}$ at 2 mA cm$^{-2}$) is given their unique intrinsic physical/chemical properties induced by their peculiar electronic configurations, multiple electron orbitals and remarkable metalloid characteristics. When paired with TiN@Fe$_2$O$_3$ anodes (0.92 mAh cm$^{-2}$ at 2 mA cm$^{-2}$), the packed full cells (stable output voltage: 1.08 V) show outstanding flexibility and weavability, achieving an impressive capacity of ~0.77 mAh cm$^{-2}$, high energy density of ~265.2 mWh cm$^{-3}$ and superb cyclic behaviors (~89.4% capacity retention even after 4000 cycles).
In addition to integrate multifunction into iron-based aqueous EES devices, the integration of such devices into other fields is also of significant interest. Chemistries enabled by ferruginous species show great promise in realizing novel cutting-edge functionalities even on the mechanically robust building materials. As a typical study focus, Julio et al. have proposed that fired bricks, one of common historical building blocks with open-up microstructures, good mechanical robustness and ~8 wt% α-Fe₂O₃ content may offer an opportunity to work as a feasible substrate for developing PEDOT-based stationary supercapacitors that easily stack into modules. Inspired by rust-assisted vapor-phase polymerization/deposition techniques, a brick’s micropores and thermal stability can be utilized for the permeation of HCl acid and EDOT monomer vapor at 160°C to control hematite dissolution/Fe³⁺ hydrolysis, and the simultaneous oxidative radical polymerization, as schematically shown in Figure 9A. A reaction diagram (Figure 9B) elaborates the detailed reaction mechanisms, where the competition between acid-catalyzed and oxidative radical polymerizations coexists; such a high H⁺ concentration would facilitate Fe³⁺ liberation on bricks for oxidative radical polymerization, meanwhile pushing forward EDOT-consumed catalyzed polymerization to form PEDOT with a low conjugation length. PEDOT-coated brick anodes can be readily connected in series (see CV profiles in Figure 9C) and encapsulated with waterproof epoxy to serve as stable stationary supercapacitor modules even when submerged underwater. With a gel electrolyte, packed supercapacitors exhibit long-lasting cyclic stability to 10000 cycles with ~90% capacitance retention. This study may add fresh values to “dirt-cheap” building materials and guide us a novel scalable way to use iron-based aqueous EES devices for smart building design.

5 | CONCLUSION AND PERSPECTIVES

In this review, we summarize the charge storage mechanisms of iron-based anodes in different aqueous EES devices, especially in some newly developed systems. The general electrode failure mechanism as well as the key routes to optimize the iron anodes are also outlined. To further promote the electrochemical performance and maximize the application potentials of iron-based aqueous EES devices, considerable collaborative efforts should be devoted in the future (Figure 10):

(i) “Recreate” viable ferruginous redox reactions in controlled electrolytes. In addition to common chemical oxidation states of Fe²⁺ and Fe³⁺, unusual valence states (like Fe⁶⁺ in the form of ferrate with a general formula of MₓFeO₄, where M is the element of K, Na, Ba, etc.) have been found to be stable in highly concentrated alkaline solutions. Once
Fe$^{6+}$-based species play a dominant role in battery systems (also named “superb-iron” battery), the total specific capacity and energy density of iron-based aqueous EES devices would be drastically increased since much more electrons can participate in oxidation–reduction conversions.$^{[163]}$ completely different from the two or three-electron transfer reaction in Ni–Fe alkaline batteries. Therefore, it
deserves to broaden the working potential window in either aqueous or even aqueous/nonaqueous hybrid electrolytes, to make full use of reversible redox couples of $\text{Fe}^0 \leftrightarrow \text{Fe}^{6+}$ for capacity promotion.

(ii) “Refresh” the electrochemical charge storage mechanisms. The concept of “hybridization/integration of battery- and supercapacitor-type energy storage behaviors” is recognized as a most adoptable way to achieve a high energy density of EES devices while not sacrificing the power performance, which has been fully verified by diverse examples such as monovalent (e.g., $\text{Li}^+$, $\text{Na}^+$, $\text{K}^+$) or multivalent ($\text{Zn}^{2+}$, $\text{Mg}^{2+}$, $\text{Al}^{3+}$) metal-ion capacitors using aqueous or nonaqueous electrolytes. These ion capacitors normally use the metallic anode via reversible metal stripping and plating, the high-specific-surface-area carbon cathode to store charges in electric double layers, as well as corresponding metal ion salts as electrolytes. The innovative development of Fe-ion hybrid EES devices is highly expected, because Fe cations (from the electrolytic salt) in the electrolyte could change their valences between $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ (or even higher chemical valence states), making further capacity contributions to full-cell systems. This would attract tremendous interest in near-future fundamental research.

(iii) “Restore” fatigued or failed ferruginous anodes by means of rapid, simple but highly effective recovery approaches. Normally, EES devices after their service lifespan need to enter into “specialized” waste streams immediately for harmlessness treatment and elemental recycling, which is rather complex, costly but very necessary for environmental protection and sustainable utilizations. However, given the current low market price and great earth abundance of iron, the resource recycling seems to be an unadvisable and rewardless choice, unless it can bring us more important benefits. In this regard, the recovery techniques of cycled iron anodes deserve our consideration. Based on the in-depth understanding of charge-storage and failure mechanisms of iron anodes, it is believed that scientists could figure out smart ways to recover these spent anodes, by effectively changing the inert $\gamma$-$\text{Fe}_2\text{O}_3$ phases into the active ones via possible physicochemical techniques, or better controlling the repetitive conversions of iron-based actives away from phase deteriorations through electrolyte engineering or any other ways.[165]

iv) “Redirect” the development orientation to environmentally benign and disposable batteries. All-iron battery systems composed of elemental Fe, ordinary nontoxic ferrous and sodium salts, as well as ferruginous phosphates (often used as food additives or raw materials for manufacturing phosphate/iron fertilizers) may hold great promise in being “absolutely green” and “ultra-low-cost” rechargeable power sources in future. Building clean and sustainable EES devices for our daily life usage is of great significance to mitigate potential issues induced from chemical hazards (e.g., heavy metals pollution, strong acid/alkali corrosion). Such redirected iron-based aqueous EES devices are predicted to save a large amount of expenditure for extra classification collection/recycling, and highly matchable for storing electricity converted from clean/renewable natural energy. Besides, extending iron-based aqueous EES devices into nonaqueous ones would be a potential development prospect. Once coupled with a proper host cathode with a high plateau potential and specific iron salt-involved electrolyte, the battery systems would deliver a superior voltage over the current level of $\approx$1.2 V, and thereby the energy density would be greatly enhanced.

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CONFLICT OF INTERESTS
The authors declare that there are no conflict of interests.

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