Unlocking the Longevity of the Iron Metal Anode

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Unlocked and inexpensive alkaline earth salt additives may hold the key to unlocking the reversibility of the iron (Fe) metal anode in mildly acidic aqueous electrolytes.

Highly reversible Fe plating and stripping can facilitate the generation of new aqueous Fe metal batteries as attractive energy storage systems due to the low cost and high capacity of Fe. Such Fe metal batteries using mildly acidic electrolytes differ from the Fe metal anode in Edison batteries, which employ a conversion reaction from Fe to Fe(OH)₂ and to Fe₃O₄ in alkaline electrolytes. Unfortunately, Fe plating/striping reactions are known for their notoriously poor reversibility. In this issue of ACS Central Science, Gao, Bedrov, and co-workers at the University of Utah have developed a new series of electrolytes that bestow the Fe metal anode with drastically improved Coulombic efficiency and enhanced plating/stripping kinetics.¹ The novel electrolytes consist of a baseline aqueous FeCl₂ electrolyte which is reinforced by the addition of either MgCl₂ or CaCl₂. Excitingly, the inclusion of these inexpensive and abundant chloride salts dramatically increases the Coulombic efficiency to a record high of >99%, thereby paving the way for the future development of long-life aqueous Fe metal batteries.

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Currently, aqueous Zn metal batteries are seen as one of the most promising technologies for large-scale energy storage. However, Fe is far more abundant than Zn, the price of Fe metal is roughly 1/43 that of Zn, and its theoretical capacities are even higher (960 mAh/g, 7557 mAh/cm³) than that of Zn (820 mAh/g, 5851 mAh/cm³).²,³ These attributes have spurred renewed interest in aqueous Fe metal batteries for grid-scale applications, and a variety of Fe-ion batteries that function via the reversible plating/striping of Fe²⁺ at the anode have been reported, where most progress has been made on the cathode side.⁴–⁶

Despite the promising characteristics of Fe metal as an anode, the reported reversibility of the Fe²⁺/Fe redox has been far from sufficient. The Coulombic efficiencies of the Fe²⁺ plating/striping process in conventional FeSO₄ or FeCl₂-based aqueous electrolytes are typically still below 91% (at applied currents of <5 mA/cm²).¹,³ The poor reversibility of the Fe metal anode redox represents one of the greatest hurdles toward the development of a practical long cycle life Fe battery. The low Coulombic efficiency can, in large part, be ascribed to the parasitic hydrogen evolution reaction (HER) that occurs at the anode surface in acidic electrolytes. The HER, which produces flammable H₂ gas, not only results in poor efficiency but can also cause increased corrosion, possible dendrite formation, and eventual cell failure. Unlike Zn metal, Fe can act as an HER catalyst, associated with a much lower HER overpotential and facile H₂ generation kinetics.¹,⁷ Therefore, devising new ways of suppressing the HER problem and...
improving Fe metal plating/stripping efficiency is imperative for the realization of practical Fe metal batteries.

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In their work, Gao et al. report encouraging results to address the issues of HER and poor Coulombic efficiency at the Fe metal anode by the addition of alkaline earth metal ions into their aqueous electrolytes. The key to their unique electrolyte design is the way in which the added cations, i.e., Mg$^{2+}$ or Ca$^{2+}$, interact with water. When the Mg$^{2+}$ or Ca$^{2+}$ ions are added to the baseline electrolyte of 0.5 M FeCl$_2$, the H-bonding network of the water becomes significantly disrupted. As illustrated by computation and experiments, the authors show that the introduced cations reduce the number of H-bonds per water molecule and increase the average H-bond length. This reduction in the number and strength of H-bonds was deemed to reinforce the covalent O–H bond of water, which renders the water less prone to reduction. Moreover, the charge-dense Mg$^{2+}$/Ca$^{2+}$ ions strongly attract water molecules into their hydration spheres and reduce the number of water molecules present in the hydration shell of Fe$^{2+}$, thereby decreasing the chance of HER when Fe$^{2+}$ is plated at the anode. These HER-suppressing characteristics allow the Fe metal anode to reach a record-high Coulombic efficiency of 99.1% in an aqueous electrolyte of 0.5 M FeCl$_2$ + 4.5 M MgCl$_2$ at a current density of 1 mA/cm$^2$. Impressively, the added MgCl$_2$ results in a dramatic 17.3% increase in efficiency as compared to the baseline 0.5 M FeCl$_2$ electrolyte. The analogous 4.5 M CaCl$_2$ + 0.5 M FeCl$_2$ electrolyte demonstrates a slightly lower, yet still good, efficiency of 98.4%. The applications of these improvements in efficiency are made apparent by the improvements in the cycling life of Fe||Fe symmetric cells, in which the Mg$^{2+}$ and Ca$^{2+}$ reinforced electrolytes demonstrate stable cycling for >250 h in contrast to cell failure after only 88.5 h for the baseline electrolyte. Of note, the significant improvements in HER suppression resulting from the addition of these inexpensive and relatively safe chloride salts are particularly attractive when compared to the flammable organic cosolvents and fluorinated salts often used to improve performance in aqueous battery systems.

Beyond suppression of HER, the excellent reversibility of the Fe metal anode achieved in these electrolytes is also made possible by an improved Fe$^{2+}$ deposition morphology. Large, compact Fe deposits were found to be plated in the new electrolytes, and less unreacted “dead” Fe was detected after stripping. In contrast, in the baseline FeCl$_2$ electrolyte, the plated morphology had a large surface area with more sites for HER to occur, and a sizable amount of dead Fe remained after the stripping process. Figure 1 schematically illustrates how the improved deposition morphology and HER-suppressing characteristics improve the reversibility of Fe metal plating/stripping in the reinforced electrolytes. Although Mg$^{2+}$ and Ca$^{2+}$ are not plated/stripped at the anode, the possibility of these ions being involved in the

![Figure 1. Schematic illustrations showing the effect of alkaline earth metal ion reinforcement on the Fe$^{2+}$ deposition/stripping performance. In the baseline electrolyte, without Mg$^{2+}$ or Ca$^{2+}$, HER is more severe, and dead iron accumulates on the anode (left). After reinforcement with Mg$^{2+}$ or Ca$^{2+}$, the HER is suppressed, and less dead iron accumulates (right). Reproduced with permission from ref 1. Copyright 2022 The Authors. Published by American Chemical Society.](https://doi.org/10.1021/acscentsci.2c00542)
reactions at certain cathode materials will need to be considered when using these electrolytes in future Fe-ion battery studies.

The simplicity and tractability of the alkaline earth metal ion reinforcement approach can likely be extended to numerous other electrolyte formulations and electrochemical systems. The results highlight the powerful effects that can be had on the physical and electrochemical properties of aqueous electrolytes via the addition of various metal ions. Therefore, beyond having developed an electrolyte that enables reversible Fe plating/stripping in aqueous electrolyte, the article by Gao, Bedrov, and co-workers exemplifies how to manipulate the properties of aqueous solutions, which can serve a plethora of different areas such as anticatalysis, Zn batteries, and supercapacitors.

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Notes
The authors declare no competing financial interest.

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