

# Recent Advances on Electrolytes for Iron-Chromium Redox Flow Batteries

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**Abstract.** The iron-chromium redox flow battery (Fe-Cr RFB) is considered the first RFB and utilizes low-cost, abundant iron and chromium chlorides as redox-active materials, making it one of the most cost-effective energy storage systems. This review first introduces the basic principles of Fe-Cr RFB and their advantages in energy storage systems, followed by an analysis of the key technical challenges they face, including low electrochemical activity of chromium ions, hydrogen evolution reaction (HER), and capacity degradation during long-term cycling. Based on these findings, the paper systematically summarizes the latest research progress on Fe-Cr RFB electrolytes, primarily including: (1) optimization of electrolyte composition; (2) application of functional additives; (3) Development of chelating electrolytes. Finally, this paper outlines future development directions for Fe-Cr RFBs aimed at enabling scalable and cost-effective energy storage.

**Keywords:** Redox flow battery; Iron-Chromium; Electrolytes.

## 1. Introduction

Renewable energy has been rapidly developed in recent years to mitigate the depletion of fossil fuel reserves and address growing environmental protection pressures.<sup>1,2</sup> Consequently, large-scale energy storage technologies have emerged as critical solutions for addressing imbalances between energy supply and demand, enhancing grid stability, and facilitating clean energy integration. Among these technologies, redox flow batteries (RFBs) have garnered significant attention due to their inherent advantages, including high safety, extended cycle life, modular power and capacity design, and environmental compatibility.<sup>3-5</sup>

Currently, all-vanadium redox flow batteries (VRFBs) have been successfully commercialized. However, the materials scarcity and price volatility of vanadium emphasize the urgent necessity to develop technologies that go beyond VRFBs.<sup>6,7</sup> Among various reported RFBs, the iron-chromium (Fe-Cr) RFB was among the first chemistries investigated because of the low cost and large abundance of chromite ore. Although the Fe-Cr electrolyte cost is low, challenges associated with Fe-Cr RFBs include crossover of metal ions, hydrogen evolution reaction (HER), and sluggish redox kinetics of  $\text{Cr}^{3+}/\text{Cr}^{2+}$ .<sup>8,9</sup> Typically, throughout the Fe-Cr RFBs operation, the operating temperature is kept at 65 °C to alleviate the issue of chromium aging phenomenon.<sup>10</sup>

The electrolyte, a core component of Fe-Cr RFBs, directly governs energy conversion efficiency, cycle stability, and operational costs.<sup>11-13</sup> Current research on electrolytes focuses on optimizing the electrochemical behavior of iron and chromium ions, enhancing electrolyte stability, improving ionic conductivity, and reducing production expenses. Recent advancements in electrolyte formulation, additive optimization, and novel supporting electrolytes have markedly boosted Fe-Cr RFB performance. For instance, introducing complexing agents and pH regulators has mitigated iron ion hydrolysis and precipitation, while refining the electrochemical reversibility of chromium ions has elevated cycling efficiency.<sup>14</sup> Concurrently, efforts to develop eco-friendly, sustainable electrolyte systems aim to address concerns regarding corrosiveness and environmental impact.

This review examines recent progress in Fe-Cr RFBs electrolytes, emphasizing composition optimization, performance enhancement strategies, and current challenges. By systematically evaluating existing studies, this work provides a theoretical foundation and technical insights to guide future electrolyte research, ultimately accelerating the adoption of Fe-Cr RFBs in energy storage systems.

## 2. Fe-Cr RFB

### 2.1 RFB principle

As depicted in **Figure 1**, RFBs employ external storage tanks to contain large volumes of electrolytes. Additionally, a key factor in many of these systems is crossover of species through the separator, which is dependent on current and membrane permeability.<sup>15</sup> During the charging cycle, electrolytes are pumped from the negative storage tank, and electrons are introduced through the anode, facilitating a reduction reaction in the electrolyte. Simultaneously, electrons are extracted at the cathode by oxidizing the electrolyte in the positive storage tank. During discharge, this process is reversed by altering the direction of electron flow, with no physical transfer of matter occurring across the electrolyte/electrode interface. All reactants involved in the reversible electrochemical reactions remain soluble and are stored in tanks, enabling scalable energy storage capacity through adjustments to reactor size and reactant selection. The electrochemical reactions predominantly occur in the solution phase, mitigating degradation of service life associated with solid-phase transformations. Additionally, the modular design of RFBs, featuring separate anolyte and catholyte reservoirs, enhances the safety of the battery system. In the event of an incident, the pumps or electron source can be entirely deactivated, and the use of water as a solvent minimizes fire risks, collectively preventing thermal runaway hazards.<sup>16, 17</sup>

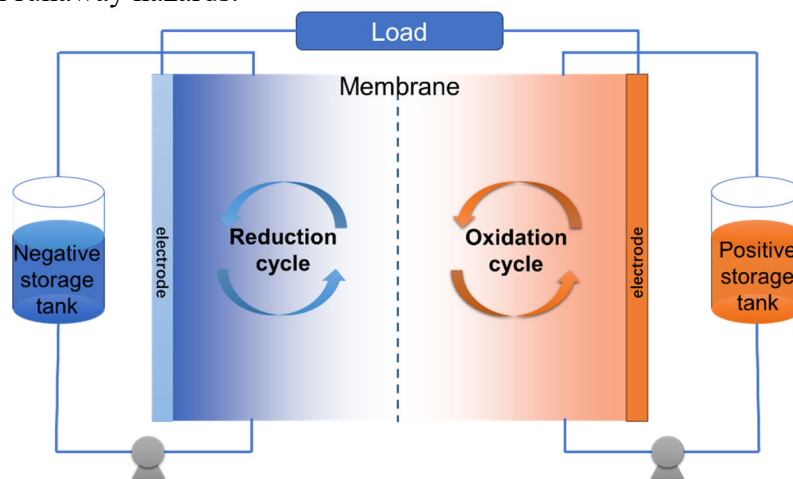
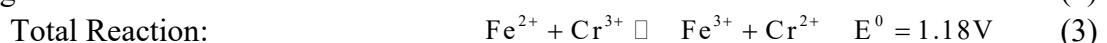
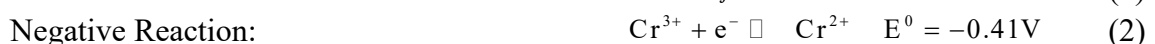


Figure 1. Schematic of A RFB.

### 2.2 Iron-chromium RFB principle

The Fe-Cr RFBs employs  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and  $\text{Cr}^{3+}/\text{Cr}^{2+}$  redox couples as the positive and negative electrode active materials, respectively, with hydrochloric acid typically serving as the supporting electrolyte. During charge/discharge cycles, the electrolyte is circulated through both half-cells via a pump system. The  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and  $\text{Cr}^{3+}/\text{Cr}^{2+}$  redox couples undergo oxidation-reduction reactions at their respective electrode surfaces. Electrons released at the positive electrode migrate through the external circuit to the negative electrode, while ionic current is maintained within the cell through ion migration in the electrolyte and proton exchange across the ion-exchange membrane. This completes the electrical circuit and facilitates the interconversion between chemical and electrical energy.

The electrode reactions of the Fe-Cr RFBs are represented by Equations (1), (2), and (3). According to the Nernst equation, the standard electromotive force at 50% state of charge (SOC) is calculated to be 1.18 V. During the charging process,  $\text{Fe}^{2+}$  ions undergo oxidation to  $\text{Fe}^{3+}$  by losing electrons, while  $\text{Cr}^{3+}$  ions are reduced to  $\text{Cr}^{2+}$  by gaining electrons. The discharge process follows the reverse reaction pathway.<sup>18</sup>



## 2.3 Problems with Fe-Cr-RFBs

Compared with other mature commercial large-scale energy storage technologies, the Fe-Cr RFBs technology offers significant advantages. Its aqueous electrolyte ensures safety by removing explosion risks, and the physical separation of electrolyte tanks from the battery pack further safeguards operations. Recently, Fe-Cr RFBs have witnessed rapid development. Nevertheless, several technical bottlenecks still impede their large-scale deployment:

(1) Poor electrochemical activity of chromium ions in anolyte: The  $\text{Cr}^{3+}/\text{Cr}^{2+}$  redox couple exhibits significantly lower activity than the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple at the cathode, disrupting the electrochemical equilibrium between the electrolytes. This discrepancy is a primary factor limiting battery performance.

(2) HER at the anode: During operation, Fe-Cr RFBs are prone to HER, which compromise normal functioning. The  $\text{Cr}^{3+}/\text{Cr}^{2+}$  redox potential (-0.41 V vs. SHE) is close to the HER overpotential on carbon electrodes. Coupled with pronounced polarization losses from sluggish kinetics, HER occurs at the anode during late-stage charging under ambient conditions, reducing energy efficiency.

(3) Severe capacity fade: Repeated charge-discharge cycles induce chemical and physical changes in electrode materials, leading to gradual degradation. Prolonged cycling also alters electrolyte composition, concentration, and pH, ultimately diminishing electrolyte performance.

## 3. Research progress of electrolytes for Fe-Cr RFBs

Past studies have focused on electrolyte component modulation (concentration or acidity optimization), additives (e.g.,  $\text{Bi}^{3+}$ ) to inhibit hydrogen precipitation, and chelate electrolytes (e.g. aminocarboxylic acid ligands) to stabilize chromium ions to synergistically enhance the performance of Fe-Cr RFBs.

### 3.1 Regulation of electrolyte components

In recent years, Fe-Cr RFBs have demonstrated promising potential for large-scale energy storage applications due to their cost-effectiveness, long cycle life, and inherent safety advantages. However, their performance remains constrained by several critical challenges, including limited electrolyte conductivity, instability of active species, and capacity degradation. To address these issues, researchers have made significant progress in enhancing energy efficiency and cycling stability through optimized electrolyte formulations, including Fe/Cr molar ratio adjustment and supporting electrolyte system modifications. The following research advances provide valuable insights into electrolyte optimization strategies:

To develop higher-performance Fe-Cr RFBs, Wang et al.<sup>19</sup> employed identical hybrid electrolytes for both electrodes. Through systematic investigations of conductivity, viscosity, and electrochemical performance under varying ion and acid concentrations, they identified the optimal electrolyte composition as 1.0 mol/L  $\text{FeCl}_2$ , 1.0 mol/L  $\text{CrCl}_3$ , and 3.0 mol/L HCl. Under these conditions, the electrolytes exhibited optimal synergistic effects in conductivity, electrochemical activity, and transport properties. Building upon these findings, Niu et al.<sup>20</sup> investigated the effects of the Fe/Cr molar ratio and hydrochloric acid concentration on the performance of Fe-Cr RFBs under a high current density of 140 mA/cm<sup>2</sup>. The study revealed that, compared to conventional commercial electrolytes (1.0 M  $\text{FeCl}_2$  + 1.0 M  $\text{CrCl}_3$  + 3.0 M HCl), the battery employing the optimized electrolyte formulation (1.25 M  $\text{FeCl}_2$  + 1.50 M  $\text{CrCl}_3$  + 3.0 M HCl) exhibited a remarkable 5.99% increase in average energy efficiency over the first 20 cycles, along with a 15.72% enhancement in discharge capacity during the initial cycle. Further experimental data demonstrated that the optimized electrolyte system exhibited superior cycling stability (Figure 1(a)). Atalaya et al.<sup>21</sup> optimized the Fe-Cr RFB electrolyte composition, identifying 2.3 M HCl with 1.25 M  $\text{FeCl}_2$  (catholyte) and  $\text{CrCl}_3$  (anolyte) as the best-performing formulation. This system demonstrated enhanced voltage efficiency and stable Coulombic efficiency under elevated temperatures, attributed to improved ionic conductivity and accelerated redox kinetics. Wang et al.<sup>22</sup> further improved performance by

increasing the HCl concentration to 3 M and operating at 65°C, achieving 82.32% energy efficiency at 80 mA cm<sup>-2</sup>. Their results highlight the critical role of electrolyte conductivity (enhanced by higher HCl) and redox activity balance (optimized Fe<sup>2+</sup>/Fe<sup>3+</sup> and Cr<sup>3+</sup>/Cr<sup>2+</sup> ratios) in enabling high-power-density operation.

To further elucidate electrolyte optimization strategies, Nico Mans et al.<sup>23</sup> systematically investigated the effects of electrolyte composition (including active material concentration, supporting electrolyte concentration, and Fe/Cr molar ratio) and supporting electrolyte type (HCl vs. H<sub>2</sub>SO<sub>4</sub>) on the performance of Fe-Cr RFBs. When employing the optimized electrolyte (1.3 M FeCl<sub>2</sub>, 1.4 M CrCl<sub>3</sub>, and 5.0 mM Bi<sub>2</sub>O<sub>3</sub> in 1.0 M HCl), the battery achieved an energy storage capacity of 24.4 Ah/L, representing a 40% enhancement compared to the conventional electrolyte (1.0 M FeCl<sub>2</sub> and 1.0 M CrCl<sub>3</sub> in 3.0 M HCl). Concurrently, the capacity decay rate was dramatically reduced from 3.0%/h to 0.3%/h, corresponding to a tenfold improvement. After optimizing the Fe/Cr concentration and ratio in the 0.5 M HCl system, the battery maintained stable performance over 50 cycles, with Coulomb efficiency of 92.3%, voltage efficiency of 78.7%, and energy efficiency of 72.6%. Comparative experiments demonstrated that the H<sub>2</sub>SO<sub>4</sub> system exhibited a significantly higher decay rate (1.6%/h) than the HCl system (0.3%/h), unequivocally identifying HCl as the superior supporting electrolyte choice. Addressing the fundamental mechanisms of capacity decay, as shown in Figure 1(b), Min Wu et al.<sup>24</sup> revealed that the capacity decay in Fe-Cr RFBs primarily stems from active ion imbalance caused by the inert Cr(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> species. By optimizing the electrolyte formulation (1 M FeCl<sub>2</sub> + 1.3 M CrCl<sub>3</sub> + 3 M HCl), the content of active Cr<sup>3+</sup> species (Cr(H<sub>2</sub>O)<sub>5</sub>Cl<sup>2+</sup> and Cr(H<sub>2</sub>O)<sub>4</sub>Cl<sub>2</sub><sup>+</sup>) was significantly increased, enabling effective matching between the Fe<sup>2+</sup>/Fe<sup>3+</sup> and Cr<sup>3+</sup>/Cr<sup>2+</sup> redox couples. Experimental results demonstrated that the optimized battery achieved an energy efficiency of 84.51% at 80 mA/cm<sup>2</sup>, representing a 2.19% improvement over the baseline electrolyte, along with a 19% reduction in capacity decay rate (7.44 vs 9.16 mAh cycle<sup>-1</sup>). Zeng et al.<sup>25</sup> utilized hydrogen gas evolved from the negative electrolyte to reduce excess Fe<sup>3+</sup> in the positive electrolyte. Their study found that when the hydrogen concentration was below 5%, the hydrogen utilization efficiency approached 100%. At a current density of 60 mA/cm<sup>2</sup> and a hydrogen concentration of 2.5%, a continuous rebalancing process could be achieved, with the rebalancing unit accounting for only approximately 1% of the total cost in the Fe-Cr RFBs system. What's more they also utilized hydrogen gas evolved from the negative electrolyte to reduce excess Fe<sup>3+</sup> in the positive electrolyte. Their study found that when the hydrogen concentration was below 5%, the hydrogen utilization efficiency approached 100%. At a current density of 60 mA/cm<sup>2</sup> and a hydrogen concentration of 2.5%, a continuous rebalancing process could be achieved, with the rebalancing unit accounting for only approximately 1% of the total cost in the Fe-Cr RFB system (Figure 1(c)).

In order to solve the issue of cross-contamination caused by concentration gradients of active species between the catholyte and anolyte, some mixed-reactant RFBs, such as the Fe-Cr RFBs, cadmium-iron RFB (ICdRFB), and vanadium-iron RFB (IVRFB), employ the same premixed reactant solution for both electrodes at 0% state of charge (SOC)<sup>26</sup>. This approach allows the capacity loss due to cross-diffusion to be mitigated by periodic remixing and redistribution of the electrolytes. The concept of using a premixed reactant solution originated from second-generation Fe-Cr RFBs systems in the 1980s, which adopted a mixed-electrolyte configuration instead of separate catholyte and anolyte solutions, where both half-cells contain chromium and iron. Furthermore, since chromium chloride (CrCl<sub>3</sub>) is typically produced from chromite ores—which naturally contain both chromium and iron—this mixed-electrolyte approach eliminates the need for costly separation processes, thereby reducing production costs. Consequently, the material expenses of the mixed electrolyte are unlikely to increase significantly and may even be lower than expected.<sup>27</sup>(Figure. 1(d)). To address the issue of ion crossover, Hagedorn et al.<sup>28</sup> proposed the concept of a hybrid electrolyte. Both the positive and negative electrolytes contain two active materials (iron and chromium), with the advantages primarily manifested in two aspects: First, the battery system no longer requires highly selective membranes. The hybrid electrolyte significantly reduces the net ion crossover rate, thereby markedly extending the operational duration of Fe-Cr RFBs. Second, for Fe-Cr RFBs electrolyte

preparation, the raw material  $\text{CrCl}_3$  is typically derived from chromite ore. The hybrid electrolyte production eliminates the cumbersome separation process of chromium and iron, reducing the production costs of active materials.

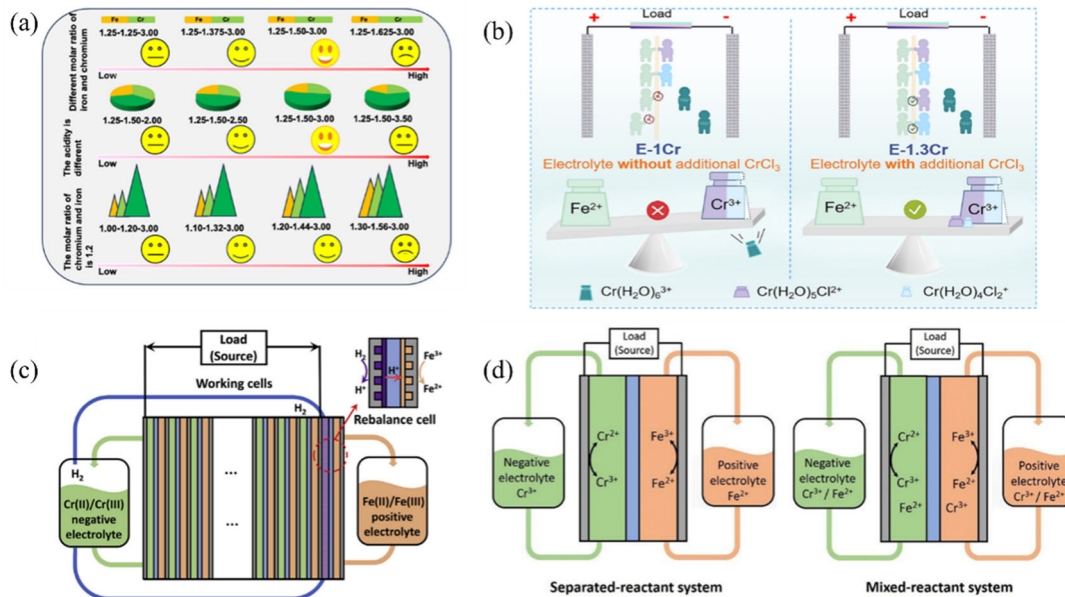


Figure 2 (a) Diagram of selecting a superior electrolyte. (b) grid Schematic diagram of operating mechanism of Fe-Cr RFBs with E-1Cr and E-1.3Cr. (c) schematic of a complete Fe-Cr RFB stack incorporating a hydrogen-ferric ion rebalance cell. (d) Schematic of the separated-reactant system and mixed-reactant system.

### 3.2 Electrolyte additives

Some scholars have optimized the electrolyte group composition and electrolyte temperature to slow down the electrolyte aging phenomenon. Recent advances in Fe-Cr RFBs have demonstrated significant performance improvements through targeted electrolyte optimization. Most notably, Wu et al.<sup>24</sup> boosted performance to 84.51% energy efficiency and 86.07% electrolyte utilization by modulating  $\text{Cr}^{3+}$  hydration states, delivering 0.773 Ah initial capacity at the same current density. These systematic optimizations of chloride-based electrolytes have collectively advanced Fe-Cr RFB technology toward practical implementation. Furthermore Cheng et al.<sup>29</sup> systematically investigated the efficacy of N-alkylamines as reactivation agents for aged  $\text{CrCl}_3$  solutions in Fe-Cr RFBs, targeting the pervasive issue of chromium speciation changes that degrade battery performance over time. Through comprehensive screening of various amine structures, they identified tetraethylenepentamine (TEPA) as the most promising candidate due to its unique molecular architecture featuring five amino groups and four ethylene spacers. TEPA's polyamine chain enables multidentate coordination with  $\text{Cr}^{3+}$  species, effectively disrupting inert  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  complexes prevalent in aged electrolytes and facilitating their conversion into electrochemically active forms such as  $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$  and  $\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2^+$ . In addition, the research team led by Wang<sup>22</sup> innovatively introduced  $\text{In}^{3+}$  as a negative electrolyte additive, demonstrating its dual functionality: (1) achieving exceptional HER suppression with a remarkably low capacity decay rate of only 0.16% per cycle, while (2) substantially enhancing the reaction kinetics of both  $\text{Cr}^{3+}/\text{Cr}^{2+}$  and  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couples. Experimental results revealed that cells with 0.01 M  $\text{In}^{3+}$  additive exhibited an energy efficiency of 77% at 200 mA/cm<sup>2</sup>, along with a 36.3% improvement in capacity retention after 140 cycles at 160 mA/cm<sup>2</sup>. This study presents a cost-effective strategy for performance optimization in Fe-Cr RFB systems (Figure 1(a) and (b)).

As shown in Figure 2(c), Li et al.<sup>30</sup> investigated guanidine hydrochloride as an additive to enhance the performance of Fe-Cr RFBs, addressing sluggish chromium reaction kinetics. Their study demonstrated that at an optimal concentration of 0.4 M, the additive reduced overpotential and achieved an energy efficiency of 80% at 55 °C, representing a 6% improvement over the baseline;

electrochemical measurements further confirmed enhanced chromium ion reactivity. Additionally, as shown in Figure 2 (d) and (e), Qiu et al.<sup>31</sup> significantly enhanced the Fe-Cr RFB by employing 0.2 M glycine as a cost-effective electrolyte additive, which stabilized cycling for 350 cycles at 140 mA cm<sup>-2</sup>. The additive optimized Cr<sup>3+</sup>/Cr<sup>2+</sup> redox kinetics via solvation-shell regulation and suppressed hydrogen evolution by displacing H<sup>+</sup> from the electrode surface. The modified system demonstrated a capacity decay of merely 1.25 mAh per cycle and energy efficiency loss of 0.018% per cycle, far surpassing the pristine electrolyte (failure at 190 cycles). On the other hand, Deng et al.<sup>32</sup> further elucidated that the imidazole additives' efficacy stems from their molecular orbital characteristics: (i) the nitrogen lone-pair electrons in imidazole rings exhibit strong  $\sigma$ -donation to Cr<sup>3+</sup>, forming Cr-N coordination bonds with binding energies of  $\sim 2.34$  eV (DFT calculations), and (ii) the additives' hydrophobic moieties create a protective interfacial layer (contact angle increased by 32 $^\circ$ ), sterically hindering water access to active sites. Electrochemical impedance spectroscopy confirmed a 41.5% increase in HER overpotential at 100 mA cm<sup>-2</sup>, while in-situ Raman spectroscopy revealed the disappearance of Cr-OH<sub>2</sub> vibrational modes at 520 cm<sup>-1</sup> upon additive introduction. These molecular-level insights explain the system's exceptional cycling stability (0.008% capacity loss/cycle over 500 cycles) and provide design principles for next-generation additives targeting transition-metal redox couples (Figure 2 (f)).

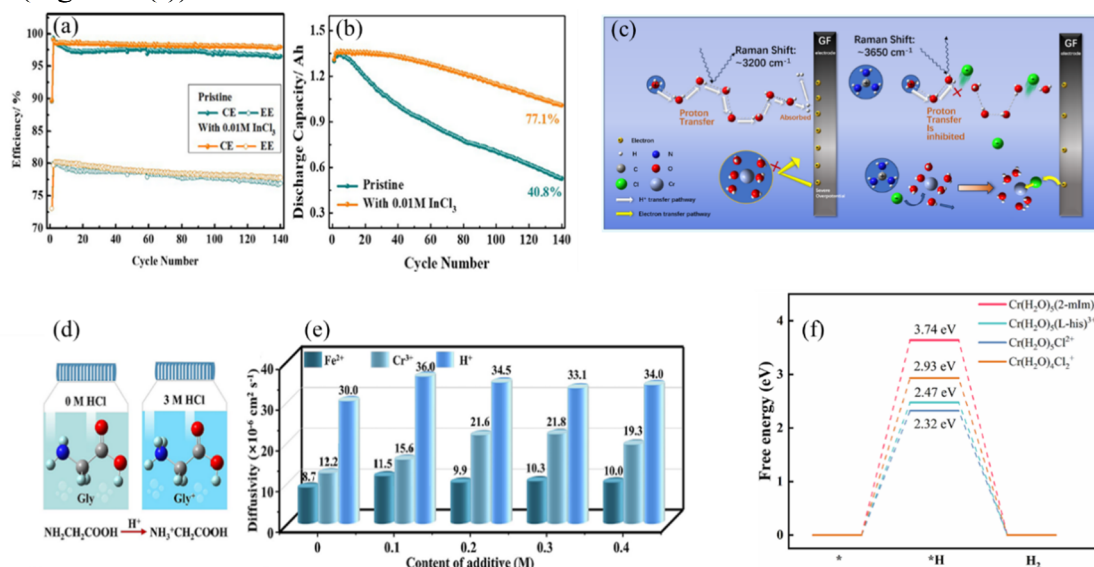


Figure 3. Cycle performance of Fe-Cr RFBs using the anolyte with and without 0.01 M In<sup>3+</sup>: (a) CE and EE, and (b) discharge capacity vs. cycle number at 160 mA cm<sup>-2</sup>. (c) Fe-Cr RFB with the guanidiniumhydrochloride as an additive for the negative electrolyte. (d) Forms of Gly in electrolytes of different acidities. (e) Calculated diffusion coefficient. (f) The energies barrier for HER in Cr(H<sub>2</sub>O)<sub>5</sub>Cl<sub>2</sub><sup>+</sup>, Cr(H<sub>2</sub>O)<sub>4</sub>Cl<sub>2</sub><sup>+</sup>, Cr(H<sub>2</sub>O)<sub>5</sub>(L-his)<sup>3+</sup> and Cr(H<sub>2</sub>O)<sub>5</sub>(2-mIm)<sup>3+</sup>.

### 3.3 Chelate electrolytes

As shown in Figure 3 (a), Jang et al.<sup>33</sup> discovered that a Cr-based negolyte coordinated with strong-field ligands could effectively mitigate the strong Jahn-Teller effects of Cr<sup>2+</sup>/Cr<sup>3+</sup>, enabling low redox potential, high stability, and rapid kinetics in Fe-Cr RFBs. The designed chelate system achieved a stable lifetime of 500 cycles with an energy density of 14 Wh L<sup>-1</sup> in a balanced full-cell configuration. With an excessive posolyte, the system reached a high energy density of 38.6 Wh L<sup>-1</sup> (single-electron redox process), offering a promising pathway for low-cost, high-performance RFBs. Except that, Chelating agents, such as ethylenediaminetetraacetic acid (EDTA), are commonly used to solubilize and stabilize metal ions for a variety of applications including agricultural fertilizer, medicine, and consumer food and health products.<sup>34</sup> (Figure 3 (b)). Furthermore, Niu et al.<sup>35</sup> developed a chromium-diethylenetriaminopentaacetic acid complex (Cr-DTPA) that demonstrates exceptional cycling stability with minimal capacity decay. As an octadentate ligand, DTPA forms a stable seven-coordinate chelation structure with chromium ions, as confirmed by comprehensive spectroscopic

characterization (NMR, FTIR, and UV-Vis). The Cr-DTPA complex exhibits excellent electrochemical activity with a redox potential of -1.145 V (vs. SCE) and remarkable reversibility. When implemented in a novel Fe-Cr RFB system pairing Cr-DTPA anolyte with  $\text{Fe}(\text{CN})_6^{3-/4-}$  catholyte, the battery achieves outstanding performance metrics: 99.0% Coulombic efficiency and 82.2% energy efficiency at  $40 \text{ mA cm}^{-2}$ . Notably, the system maintains unprecedented cycling stability over 160 cycles without performance degradation, representing the best-reported stability among contemporary Fe-Cr RFBs. This work establishes chelation engineering as an effective strategy to address chromium anolyte deactivation while significantly enhancing battery durability (Figure 3 (c)).

As shown in Figure 3 (d), Bamgbopa et al.<sup>36</sup> developed an innovative nonaqueous iron-chromium acetylacetonate redox flow battery system featuring: (1) paired Fe(III)/Cr(III) redox couples, (2) a hybrid Nafion/SiO<sub>2</sub> ion-conductive membrane, and (3) an optimized 84/16 vol% acetonitrile/1,3-dioxolane electrolyte. This design achieves remarkable 3 V fast-charging capability while maintaining 99% Coulombic efficiency, 53% energy efficiency, and stable performance over 50 cycles, offering a promising solution to the challenges of high cost and low efficiency in conventional nonaqueous RFBs. Apart from this, Robb et al.<sup>37</sup> demonstrated that incorporating metal chelators (particularly EDTA for chromium) in Fe-Cr RFB electrolytes simultaneously regulates redox potentials (shifting  $\text{Cr}^{3+}/\text{Cr}^{2+}$  from -0.41 to -0.99 V vs. SHE at neutral pH), optimizes solubility/pH, suppresses membrane crossover, and enhances chromium redox kinetics by  $10^5$ . Waters et al.<sup>38</sup> demonstrated that chelation significantly enhances the performance of Fe-Cr RFBs, with  $\text{Fe}^{3+/2+}$ -DTPA and Cr-PDTA complexes exhibiting exceptional electrochemical properties at pH 9. The optimized system achieved remarkable metrics: 1.35 M iron concentration ( $36.2 \text{ Ah L}^{-1}$  capacity), near-quantitative efficiency, 1.2 V cell potential, and  $216 \text{ mW cm}^{-2}$  peak power density, highlighting the critical role of molecular design in advancing flow battery technology (Figure 1(e)).

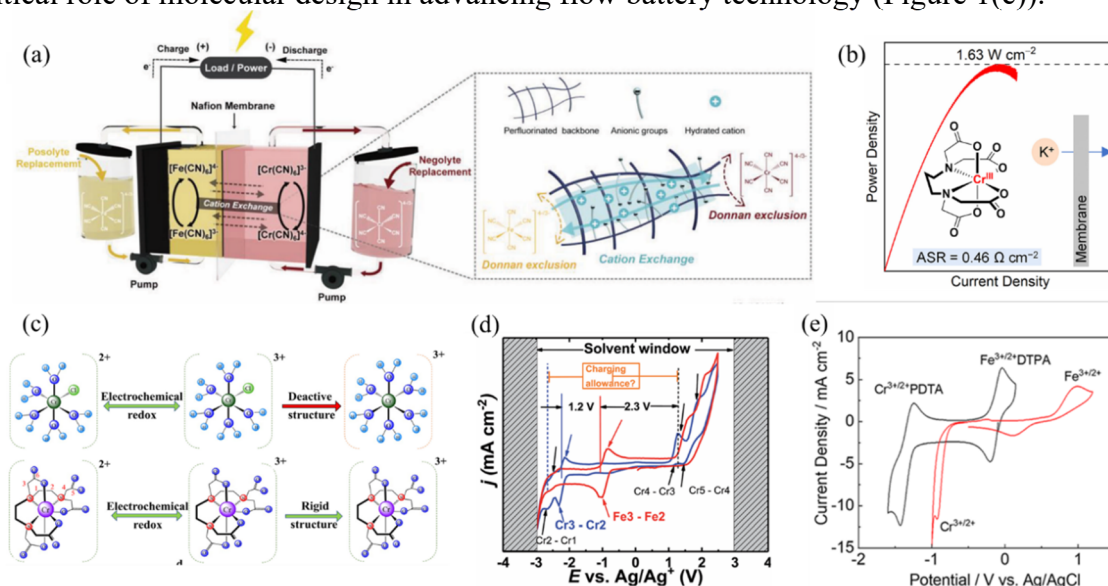


Figure 4. (a) Cell schematic of the negolyte of  $[\text{Cr}(\text{CN})_6]^{4-/3-}$  paired with the posolyte of  $[\text{Fe}(\text{CN})_6]^{4-/3-}$ . (b) Power density of Cr(PDTA) RFB. (c) Coordination structure change diagram of  $\text{CrCl}_3$  anolytes and CrDTPA anolytes. (d) Cyclic voltammograms of  $\text{Fe}(\text{acac})_3$  and  $\text{Cr}(\text{acac})_3$  with 0.05 M TEABF<sub>4</sub> as the support electrolyte in acetonitrile at a platinum electrode. (e) Cyclic voltammogram of 50 mM CrPDTA / FeDTPA (black) with 0.25 M KBi at pH 9.0 and 50 mM CrCl<sub>3</sub> / FeCl<sub>2</sub> (red) in 3 M HCl performed on a glassy carbon electrode at  $100 \text{ mV s}^{-1}$ .

## 4. Conclusions

Fe-Cr RFBs are promising for large-scale energy storage, featuring low-cost electrolytes, high safety, long cycle life, and environmental friendliness. However, they face key challenges: sluggish

$\text{Cr}^{3+}/\text{Cr}^{2+}$  redox kinetics, energy loss from hydrogen evolution, and capacity decay due to ion imbalance in long-term cycling. This paper systematically reviews recent advances in Fe-Cr RFB electrolytes, focusing on composition optimization (Fe/Cr ratio and supporting electrolyte concentration), functional additives (like  $\text{In}^{3+}$  and imidazoles) for HER suppression and chromium activity enhancement, and chelating electrolytes (e.g., EDTA, DTPA) for redox potential regulation and stability improvement. It also discusses existing technical bottlenecks and engineering challenges.

To advance Fe-Cr RFBs, three key research directions are proposed: (1) Developing catalytic additives to enhance  $\text{Cr}^{3+}/\text{Cr}^{2+}$  redox kinetics; (2) Designing efficient HER inhibitors (organic/nanostructured materials) to minimize hydrogen evolution at electrodes; (3) Creating ultra-stable chromium complexes using hydrolysis-resistant multidentate ligands, coupled with in situ characterization to understand degradation mechanisms. These synergistic approaches address critical challenges in reaction kinetics, side reactions, and long-term stability, potentially overcoming existing technical barriers for commercial-scale Fe-Cr RFBs applications.

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