All-iron redox flow batteries

Working principle and recent developments

Department of mechanical and materials engineering

Bachelor's thesis

Author:
Aapeli Hyvärinen

1.4.2025

Turku

Bachelor's thesis

Subject: Materials engineering
Author: Aapeli Hyvärinen
Title: All-iron redox flow batteries – Working principle and recent developments
Supervisor: Dr. Jerzy Jasielec
Number of pages: 30 pages
Date: 1.4.2025

Abstract

All-iron redox flow batteries (AIRFBs) are a promising energy storage solution due to their low cost, safety, and abundance of raw materials. Their ability to decouple energy capacity from power output makes them highly scalable for grid applications. Traditional AIRFBs, however, face challenges such as limited charge-discharge depth, hydrogen evolution, and membrane selectivity issues, which hinder their commercial adoption.

Recent developments in electrolyte formulations, electrode engineering, and membrane technologies have improved efficiency, cycle life, and cost-effectiveness. The introduction of all-soluble AIRFBs (ASAI-AIRFBs) has further enhanced system stability by eliminating solid-phase deposition, improving electrolyte utilization, and increasing energy density. Additionally, innovative additives like 1-ethyl-3-methylimidazolium chloride (EMIC) have demonstrated enhanced electrolyte stability and reduced unwanted side reactions, contributing to long-term operational reliability.

This thesis provides a review of the working principles of AIRFBs, key technological advancements, and ongoing challenges in the field. The study also highlights the potential integration of AIRFBs with renewable energy sources, addressing their role in facilitating sustainable energy storage solutions [1].

Key words: AIRFB, RFB, energy storage, flow battery, sustainable solutions

Table of contents

Used abbreviations:

AEM - Anion exchange membrane

AIRFB - All-iron redox flow battery

ASAI-AIRFB - All-soluble all-iron redox flow battery

CE - Coulombic efficiency

CNT - Carbon nanotube

DEIPA - Diethanolisopropanolamine

DFT - Density Functional Theory

EE - Energy efficiency

EMIC - 1-ethyl-3-methylimidazolium chloride

FO - Flow-over (configuration)

FT - Flow-through (configuration)

HC - Hard carbon

HER - Hydrogen evolution reaction

LIB - Lithium-ion battery

MWCNT - Multi-walled carbon nanotubes

NTMPA - Nitrilotri(methylphosphonic acid)

PAN-GF - Polyacrylonitrile-based graphite felt

RFB - Redox flow battery

TEOA - Triethanolamine

TIPA - Triisopropanolamine

VE - Voltage efficiency

VRFB - Vanadium redox flow battery

1 Introduction

1.1 Energy storage

The urgent shift towards renewable energy sources highlights the increasing need for reliable energy storage solutions. Solar and wind power generate fluctuating electricity production, requiring effective storage systems to balance the grid. It is crucial to develop efficient, large-scale systems that can store surplus energy until it is needed.

Pumped hydro-storage is currently the most widely deployed large-scale energy storage solution. However, electrochemical energy storage is rapidly gaining traction, with redox flow batteries (RFBs) emerging as a promising alternative.

1.2 RFBs

RFBs use liquid electrolytes stored in external tanks [2]. This system allows energy capacity to be scaled by increasing electrolyte volume. Power output is determined by the size of the stack. The use of liquid electrolytes minimizes structural wear and extends operational lifespan. RFBs also offer rapid charge-discharge cycles and extended idle periods. Additionally, the ability to remain in an idle state without self-discharge makes them reliable for intermittent renewable energy integration and backup power applications.

These attributes make them particularly well-suited for grid-scale applications, where large amounts of energy must be stored efficiently and safely [1]. With cost-effectiveness, modularity, and long-term stability, RFBs represent an important step toward sustainable energy storage.

Safety aspect applies especially with all-iron RFBs (AIRFBs) since they do not contain elements that are harmful to the environment. Moreover, iron is abundantly available unlike lithium and vanadium, for example. AIRFBs use water-based electrolytes. Therefore, fire hazards associated with organic solvents do not occur [2].

1.3 Scope and objectives

AIRFBs have gained increasing attention as a cost-effective and scalable solution for large-scale energy storage, particularly in applications requiring stationary long-duration storage. Unlike conventional lithium-ion batteries (LIBs) and vanadium RFBs (VRFBs), AIRFBs

offer great advantages in terms of cost, safety, and resource availability. However, challenges such as electrolyte stability, side reactions, and capacity decay still hinder their widespread application. The introduction of new technologies, such as all-soluble AIRFBs (ASAI-AIRFBs), aims to overcome these challenges.

The scope of this thesis is to examine the working principles and recent developments of AIRFBs. The thesis aims to provide a comprehensive overview of the electrochemical mechanisms that run AIRFBs, detailing the redox couples in charge and discharge cycles. It investigates recent advancements in materials science, particularly improvements in membrane selectivity, electrode surface engineering, and electrolyte formulations that enhance efficiency and durability.

To assess overall system performance, key indicators such as Coulombic efficiency (CE), which reflects charge retention, voltage efficiency (VE), which compares charge and discharge voltages, and energy efficiency (EE), which represents the total energy conversion effectiveness, are considered. Finally, this thesis explores the potential for large-scale commercialization by analysing scalability challenges, and the integration of AIRFBs with renewable energy sources.

By addressing these topics, this thesis seeks to contribute to the ongoing research and development efforts aimed at optimizing AIRFB.

2 AIRFBs

2.1 System components

AIRFBs operate through a system composed of an anolyte and catholyte storage tanks, a flow cell stack, an ion-conducting membrane, and an electrolyte circulation system. These components work together to enable continuous circulation of soluble iron-based electrolytes between the electrodes, where redox reactions facilitate energy storage and release.

Within the electrochemical cell, carbon-based electrodes, typically made of graphite or carbon felt, provide a large surface area to support these reactions. The anolyte and catholyte, stored separately in tanks, are pumped through the cell, allowing charge transfer to occur efficiently at the electrode-electrolyte interface.

A key feature of AIRFBs is their ability to decouple energy storage capacity from power output, which is determined by the electrolyte volume and the electrochemical cell's active area, respectively. This makes AIRFBs highly scalable, as increasing storage capacity only requires larger electrolyte reservoirs rather than modifications to the electrode stack [1]. A simplification of traditional AIRFB composition is represented in Figure 1.

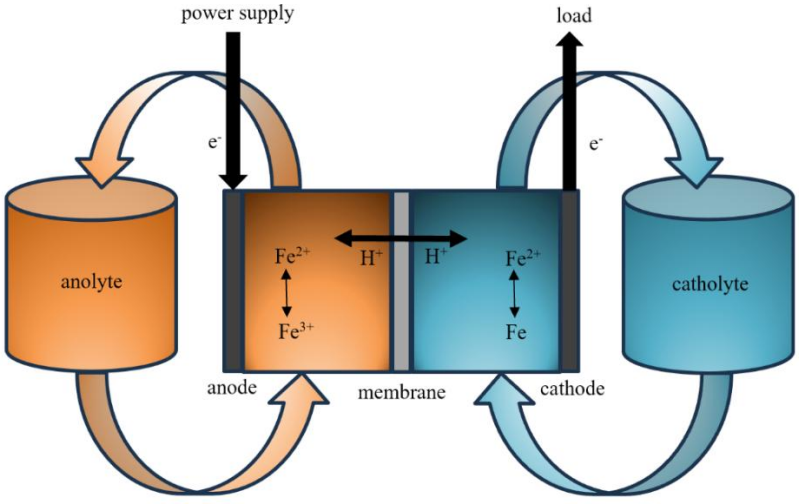

Figure 1. A traditional AIRFB.

2.2 Electrochemical reactions

2.2.1 Traditional AIRFBs

The fundamental electrochemical processes in AIRFBs involve both homogeneous and heterogeneous redox reactions. AIRFBs utilize the Fe^{2+}/Fe^{3+} and Fe/Fe^{2+} redox couples to

enable charge and discharge cycles. The positive half-cell operates through the Fe^{2+}/Fe^{3+} redox couple, where Fe^{2+} is oxidized to Fe^{3+} during charging and reduced back to Fe^{2+} during discharge. The reversible reaction can be written as:

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^{-}. \quad (1)$$

The reaction occurs in solution, ensuring a fast and reversible process with minimal kinetic limitations [2].

The negative half-cell operates through a different mechanism involving the Fe^{2+}/Fe redox couple, which requires the deposition and dissolution of solid metallic iron onto the electrode surface:

$$Fe \rightleftharpoons Fe^{2+} + 2e^{-}. \quad (2)$$

Unlike the positive half-cell, this plating-stripping reaction introduces additional challenges such as charge transfer resistance, nucleation and growth kinetics, and competitive side reactions like hydrogen evolution reaction (HER).

One of the challenges related to electrochemical reactions in AIRFBs is maintaining the required pH conditions for stable operation. The Fe^{3+} ions in the catholyte require an acidic environment (pH < 3) to prevent hydrolysis and the formation of $Fe(OH)_3$ precipitates. The hydrolysis reaction can be expressed as:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^{+}. \quad (3)$$

In contrast, the anode environment must be more basic to avoid the HER:

$$2H^{+} + 2e^{-} \rightarrow H_2, \quad (4)$$

which otherwise competes with iron deposition.

This pH incompatibility creates an operational challenge that often necessitates additional balancing systems [3].

2.2.2 ASAI-AIRFBs

ASAI-AIRFBs represent an advancement over traditional AIRFBs, addressing major challenges such as solid-phase deposition and limited cycle life. Unlike conventional AIRFBs, which suffer from the challenges with iron plating and stripping at the negative

electrode, ASAI-AIRFBs utilize fully soluble iron complexes in both half-cells. This approach improves charge/discharge reversibility and enhances cycle stability. A comparison between ASAI-AIRFBs and deposition-type AIRFBs highlights the advantages of the former, such as tuneable cell voltage, higher electrolyte utilization (up to 100% vs. <50% in deposition-type), and increased energy density [1].

A key innovation in ASAI-AIRFBs is the use of organic ligands to coordinate iron ions, significantly improving their solubility and stability. In traditional AIRFBs, free Fe^{3+} ions in the catholyte can undergo hydrolysis, leading to $Fe(OH)_3$ precipitation (see eq. 3). This issue is mitigated in ASAI-AIRFBs by employing iron-ligand complexes, such as triethanolamine (TEOA), nitrilotri(methylphosphonic acid) (NTMPA), and ferro-/ferricyanide complexes, which stabilize iron ions across a broader pH range. Particularly, Fe-CN complexes have demonstrated superior electrochemical stability in alkaline conditions [4]. These ligands suppress unwanted side reactions and optimize battery performance by shifting the redox potential of Fe^{3+}/Fe^{2+} [1].

The positive half-cell of ASAI-AIRFBs typically employs the Fe^{3+}/Fe^{2+} redox couple, where iron is complexed with ligands to enhance solubility and electrochemical stability:

$$Fe(L)^{3+} + e^- \rightleftharpoons Fe(L)^{2+} \tag{5}$$

where L represents an organic ligand that stabilizes the iron species in solution.

The negative half-cell, in contrast to traditional AIRFBs that rely on Fe^{2+}/Fe metal deposition, uses soluble Fe^{2+}-ligand complexes instead. This prevents solid-phase deposition, eliminates dendrite formation, and enhances electrode longevity [5]. In systems that use ferricyanide as the catholyte, the redox reaction follows:

$$[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}. \tag{6}$$

This reaction takes place in an alkaline medium, offering improved electrochemical reversibility and a reduced risk of HER (see eq. 4), which commonly affects traditional iron-based redox systems [1].

While ASAI-AIRFBs offer numerous advantages, several challenges remain. One of the most critical issues is ligand crossover through the ion-exchange membrane, leading to capacity imbalance and performance degradation. [5].

3 Materials and methods

3.1 Electrolyte

The electrolyte in AIRFBs plays a crucial role in enabling efficient battery performance. The electrolyte serves as a medium for ion transport and facilitates the reversible redox reactions of iron species at the electrodes during charge and discharge cycles. AIRFBs utilize aqueous iron-based electrolytes.

One of the primary challenges in AIRFB electrolyte formulation is balancing the pH to prevent unwanted side reactions. Ferric ions (Fe^{3+}) are prone to hydrolysis in solutions with a pH above 3, forming insoluble ferric hydroxide ($Fe(OH)_3$) precipitates (see eq. 3), which can reduce battery efficiency and clog the membrane. Conversely, in strongly acidic conditions, HER (see eq. 4) competes with iron deposition.

To address this challenge, stabilizing additives, like 1-ethyl-3-methylimidazolium chloride (EMIC), can be introduced. Adding EMIC to the electrolyte system effectively resolves the low solubility of $FeSO_4$ in water. According to Density Functional Theory (DFT) calculations, a quantum mechanical method for studying molecular electronic structures and interaction energies, EMI^+ strengthens the interaction between sulfate ions and water molecules. Specifically, DFT calculations reveal that EMI^+ can form stabilizing electrostatic and hydrogen bonding interactions with sulfate anions. It reduces their tendency precipitate. This leads to improved solubility of $FeSO_4$ in the electrolyte, ensuring a more stable and homogeneous solution, which is critical for the efficient operation of the battery system [3].

The conductivity of the electrolyte is also a critical parameter influencing battery performance. High iron salt concentrations increase ionic conductivity, reducing internal resistance and improving charge transfer kinetics. However, high concentrations also increase viscosity, which limits ion mobility. Studies show that while 1 M $FeSO_4$ electrolyte provides sufficient conductivity, 2 M $FeSO_4$ significantly enhances both ionic conductivity and overall battery performance. The addition of 0.1 M EMIC further improves solubility without negatively impacting reaction kinetics. Therefore, to achieve strong ionic conductivity, the $FeSO_4$ concentration should be at least 2 M, while balancing solubility and viscosity is essential for optimizing AIRFB system efficiency.

Membrane compatibility also affects electrolyte performance. Unlike in VRFBs, where expensive ion-exchange membranes are required, AIRFBs can function with more affordable microporous membranes due to the similar ionic species in both half-cells [3].

3.2 Electrodes

Electrodes facilitate electron transfer and support the electrochemical reactions that enable energy storage and release. The most used electrode materials in AIRFBs are carbon-based, such as graphite felt, carbon paper, and carbon cloth. These materials are favoured for their high surface area, good electrical conductivity, and chemical stability in acidic environments.

The electrodes in AIRFBs provide an interface for the Fe^{2+}/Fe^{3+} redox reaction in the positive half-cell (see eq. 1) and the Fe^{2+}/Fe^{0} reaction in the negative half-cell (see eq. 2). During charging, Fe^{2+} ions oxidize to Fe^{3+} at the anode, while Fe^{2+} ions reduce to metallic iron (Fe^{0}) at the cathode. This process is reversed during discharge, allowing energy to be retrieved efficiently. The effectiveness of the electrodes depends on surface area, porosity, and the presence of functional groups that can boost catalytic activity and charge transfer efficiency.

A key challenge in AIRFB electrode development is reducing polarization losses from charge transfer resistance and mass transport limits. To address this, various surface modifications have been explored, including thermal activation, nitrogen doping, and various coatings. These treatments aim to boost electrode wettability, improve electron conductivity, and promote more uniform iron deposition and dissolution [3].

Optimizing electrode materials is essential for improving the overall performance and longevity of AIRFBs. One of the primary objectives is to achieve uniform iron deposition across the electrode structure, preventing localized current density fluctuations that can result in soft short circuits and membrane clogging. Ensuring even iron distribution is particularly important in carbon felt electrodes, where variations in particle deposition can impact charge transfer efficiency and long-term stability.

Research suggests that electrolyte additives such as EMIC can enhance the wetting properties of carbon felt, improving electrolyte penetration and promoting more homogeneous iron deposition. However, while EMIC improves electrolyte interaction with the electrode structure, its precise influence on iron redox kinetics and particle morphology requires further investigation [1].

A key factor in electrode design is maintaining structural integrity over long cycles. Conventional graphite felt electrodes degrade over time as iron accumulates, reducing electrochemical activity. Newer materials, such as carbon nanotube-enhanced electrodes and hybrid composite electrodes, offer improved mechanical stability and better resistance to electrode passivation [3]. The integration of three-dimensional electrode architectures has also shown promise in optimizing the stability and electrolyte flow distribution.

The three-dimensional electrodes provide a porous network that allows for improved mass transfer and higher active surface area. Furthermore, these structures can be fabricated using materials such as foams, biomass-derived carbons, and electrospun fibers. Each offers unique advantages in terms of conductivity, stability, and catalytic activity. By employing such electrodes, the overall reaction kinetics within RFBs can be enhanced, reducing internal resistance and increasing overall EE.

The flexible design of 3D electrodes allows for customized structural modifications, such as functional doping and adding nanomaterials, to improve redox reaction sites and ion movement. For instance, incorporating metal-based, carbon-based, or composite electrocatalysts into 3D electrodes has been shown to stabilize the surface charge distribution. These advancements contribute to a more homogeneous and durable electrode architecture, which is critical for long-term operation in RFBs. [5]

3.3 Membrane

Membrane serves as a selective barrier that prevents the crossover of active species while allowing charge-balancing ions to pass through. Its role is essential in maintaining ionic conductivity and ensuring efficient battery operation. For long-term cycle stability, the membrane must be mechanically strong, chemically stable, and resistant to degradation under continuous electrochemical cycling [6].

Typically, ion-exchange membranes or microporous separators are used to maintain charge balance and control ion transport in AIRFBs. Cation-exchange membranes, such as Nafion, facilitate the transport of protons (H^+) between compartments, ensuring charge neutrality while preventing iron species from crossing over [3]. While Nafion-based membranes are widely used, alternative materials such as sulfonated polyethylene styrene–divinylbenzene membranes have been investigated to reduce costs and enhance chemical stability. Anion-exchange membranes have also been explored in some configurations to further regulate iron

transport mechanisms Additionally, surface modifications using nanoparticle coatings and composite materials have been studied to improve membrane selectivity and suppress competing reactions like HER (see eq. 4) [1].

In AIRFBs, one of the main challenges associated with membranes is the potential for iron ion crossover, which can lead to electrolyte contamination, and long-term capacity degradation. To prevent this, membranes must exhibit high selectivity, allowing only the desired ions (H^+) to pass through while effectively blocking Fe^{2+} and Fe^{3+} migration. Another critical requirement for membranes is chemical and mechanical stability. They must withstand long-term exposure to electrolyte solutions and maintain structural integrity under cycling conditions. High conductivity is also essential to minimize ohmic losses.

In AIRFBs, membrane degradation poses a challenge to performance and durability. One of the primary failure mechanisms is the uncontrolled growth of iron deposits, which can penetrate the membrane and lead to internal short circuits. Additionally, maintaining a stable pH gradient across the membrane is important, as imbalances can cause $Fe(OH)_3$ precipitation (see eq. 3). This buildup would increase membrane resistance, leading to higher cell impedance and reduced efficiency [3].

Research efforts have focused on developing advanced membrane materials with improved selectivity and resistance to iron crossover. Potential solutions include chemically modified ion-exchange membranes, composite structures, and surface coatings designed to enhance durability [6].

3.4 Cell design

The design of an AIRFB cell involves the integration of electrodes, a membrane separator, and electrolyte flow channels into a compact and efficient configuration. The flow cell is typically assembled with two carbon felt electrodes, which are pressed against a microporous membrane.

The electrolyte is stored in external reservoirs and circulated through the cell using peristaltic pumps. The flow dynamics play an important role in battery performance, as optimizing electrolyte circulation enhances CE and EE. Optimized flow reduces concentration polarization and improves mass transport at the electrode surface.

Flow field design is another critical factor in cell assembly. AIRFBs can employ either flow-through (FT) or flow-over (FO) configurations. In the FT configuration, the electrolyte flows through a porous electrode from one side to the other. In the FO configuration, electrolytes flow over a structured flow field before diffusing into the electrode layer. Studies indicate that the FO configuration with thin carbon papers achieves higher power density and EE compared to the FT design using graphite felt [1]. FT and FO configurations are depicted in Figures 2 and 3.

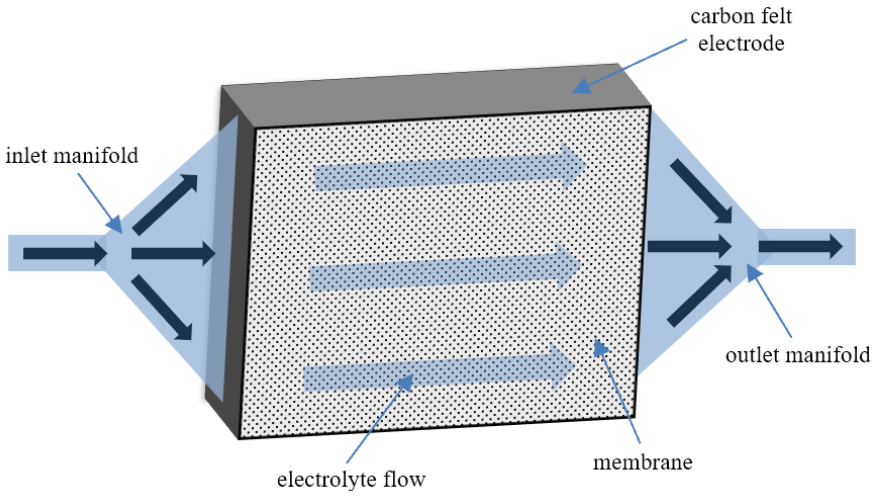

Figure 2. FT configuration.

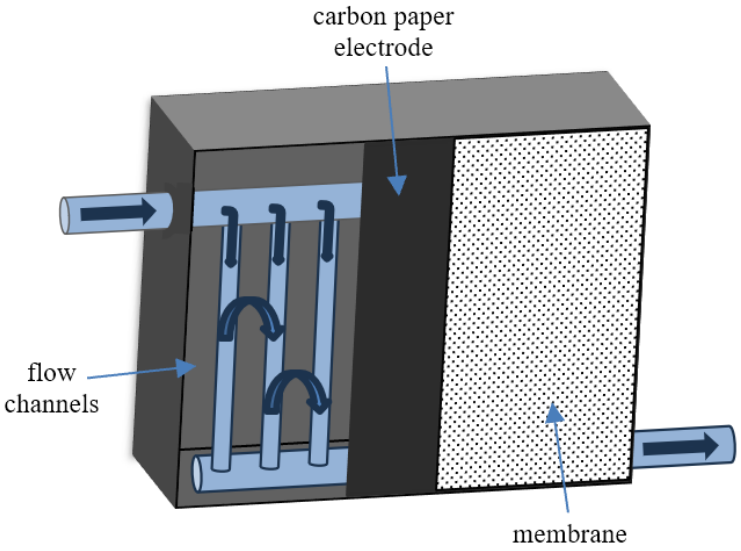

Figure 3. FO configuration.

4 Recent developments

4.1 Advancements in electrolyte formulations

Recent advancements in electrolyte formulations for AIRFBs have primarily focused on improving efficiency, reducing internal resistance, and minimizing unwanted side reactions such as HER. One of the breakthroughs in this area is the incorporation of organic ligands and additives, which help extend electrolyte stability and prolong battery lifespan [2].

Another critical factor in electrolyte optimization is pH management. To address this, studies have explored the use of buffering agents such as ascorbic acid and ammonium chloride, which expand the operational pH range and prevent $Fe(OH)_3$ (see Eq. 3) formation without compromising electrochemical activity [7].

4.1.1 Organic electrolytes

The degradation of aqueous organic electrolytes and ligand cross-contamination leads to a decline in the battery's capacity over time. Researchers have been exploring the use of organic ligands to coordinate with iron, aiming to create more robust and stable electrolytes.

A more stable anolyte was achieved by employing the bulky triisopropanolamine (TIPA) in $FeSO_4$-based electrolytes. TIPA provides strong steric hindrance, which limits ligand dissociation and prevents ligand crossover through the membrane. Compared to ligands such as triethanolamine (TEA) and diethanolisopropanolamine (DEIPA), TIPA has demonstrated superior electrochemical stability. Additionally, TIPA is relatively inexpensive and readily available, making it an attractive option for large-scale AIRFB development [4].

Recent research has further confirmed that TIPA's steric effects reduce electrolyte contamination, thereby minimizing capacity decay. Molecular dynamics simulations indicate that TIPA forms a stable coordination structure with Fe^{3+}, replacing water molecules in the solvation shell and reducing hydrolysis-induced side reactions (see eq. 3). Compared to previously used ligands, TIPA demonstrates a stronger Fe-O coordination bond, leading to a more stable electrolyte composition and extended battery lifespan.

AIRFBs utilizing $FeSO_4$-TIPA as the anolyte have shown long-term stability, exceeding 1800 cycles with minimal capacity loss while maintaining high EE. Further electrolyte optimization (0.4 M Fe-TIPA) extended stability to 2490 cycles, demonstrating its potential for long-term

operation. In contrast, Fe-TEA and Fe-DEIPA anolytes suffered significant degradation after only 464 and 890 cycles, respectively, due to ligand crossover and oxidative degradation at the cathode [8,9].

Cyclic voltammetry measurements have confirmed that Fe-TIPA exhibits superior electrochemical kinetics compared to conventional iron-based electrolytes. The Fe^{3+} diffusion coefficient in the TIPA complex was measured at 1.10×10^{-3} $cm^2 \cdot s^{-1}$ for oxidation and 1.44×10^{-3} $cm^2 \cdot s^{-1}$ for reduction, significantly higher than previous aqueous organic iron electrolytes. This enhanced charge transfer efficiency reduces polarization losses and improves power density, making AIRFBs more efficient and commercially viable [4].

4.1.2 Inorganic electrolytes

An alternative approach to improving AIRFB performance is the use of inorganic electrolytes, focusing particularly on iron plating-stripping kinetics in the negative half-cell. One of the breakthroughs has been the introduction of sodium bisulfite ($NaHSO_3$) as an additive, which has shown great improvements in iron deposition and dissolution.

This system utilizes a $FeCl_2$-based electrolyte rather than $FeSO_4$, with the following composition: 0.5 M $FeCl_2$, 3.0 M NaCl, and 10 mM citric acid (H_3Cit). The primary benefit of $NaHSO_3$ is its role as an oxygen scavenger. It prevents unwanted oxidation of Fe^{2+} to Fe^{3+} and minimizes the formation of insoluble $Fe(OH)_3$ precipitates (see eq. 3). Additionally, $NaHSO_3$ facilitates the formation of a $FeHSO_3^+$ complex, which enhances iron ion mobility. This allows for a more uniform distribution of iron, improves plating-stripping behaviour and prevents metallic filament formation.

$NaHSO_3$ reduces charge transfer resistance at the electrode-electrolyte interface, leading to lower polarization losses. Electrochemical characterization using linear sweep voltammetry (LSV) and rotating disk electrode (RDE) experiments confirmed that the presence of $NaHSO_3$ nearly doubled cathodic currents. This demonstrates a notable improvement in iron deposition kinetics. These findings highlight the potential of $NaHSO_3$ as a simple yet highly effective additive for optimizing AIRFB electrolytes [10].

4.1.3 External magnetic field

Another innovative approach to improving electrolytes in AIRFBs is the application of an external magnetic field. It has been shown to boost mass transfer and increase ion mobility

within the electrolyte. By applying a strong neodymium iron boron magnet with a magnetic field strength of approximately 0.2 T, researchers observed a marked improvement in ion distribution and charge transfer efficiency.

The mechanism behind the improvement is the Lorentz force, a fundamental force in electromagnetism that acts on charged particles moving within a magnetic field. In the electrolyte, this force influences the motion of Fe^{2+} and Fe^{3+} ions, causing them to follow curved trajectories rather than moving in a straight line. This promotes more uniform mass transfer, reduces concentration gradients near the membrane, and prevents localized ion loss, which is a common issue in traditional AIRFB configurations. Additionally, the magnetic field allows solid particles in the electrolyte to form a conductive network that lowers charge transfer resistance.

Experimental data demonstrated that combining an optimized electrolyte formulation with an external magnetic field increased the average discharge voltage from 1.09 V to 1.23 V. This enhancement is attributed to improved electrochemical kinetics, as a more homogeneous ion distribution allows for more efficient electron exchange at the electrode surface [11].

4.2 Innovations in electrode/membrane technologies

4.2.1 Composite electrodes

Optimized electrode materials ensure effective charge transfer while minimizing HER (see Eq. 4). Recent advancements have focused on the development of composite electrodes that exhibit improved electrocatalytic activity [2].

One promising approach is the integration of hard carbon-based composites, which provide enhanced stability in acidic environments and offer a broader electrochemical stability window compared to conventional graphite. Hard carbon (HC) electrodes exhibit superior resistance to degradation and reduce the occurrence of side reactions. When combined with niobium pentoxide, for example, these materials achieve lower overpotentials and enhanced electron transfer rates, making them highly effective for long-term operation.

Further studies have demonstrated the benefits of niobium-doped carbon electrodes, where various niobium oxide forms (NbO, NbO_2, and δ-Nb_2O_5) have been incorporated into carbon matrices to enhance electrocatalytic activity. Among these, the HC-Nb10C90 composition

(containing 10% Nb_2O_5 in HC) has shown the highest redox activity for Fe^{3+}/Fe^{2+} while maintaining excellent resistance to electrode degradation.

Beyond niobium oxides, various composite materials have been explored to improve the performance of AIRFBs. One notable approach is the integration of vanadium pentoxide (V_2O_5) with carbon spheres (V_2O_5-CS), which enhances electron mobility and increases the reversibility of the redox reaction. The oxygen-rich V_2O_5 sites improve charge transfer, while carbon spheres provide structural reinforcement and enhance electrical conductivity.

Another promising modification involves nitrogen-doped carbon electrodes, which facilitate stronger interactions between Fe^{3+}/Fe^{2+} ions and the electrode surface, reducing charge transfer resistance. Additionally, biomass-derived carbon materials have gained interest due to their high porosity and tuneable surface chemistry, allowing for enhanced ion transport and improved electrolyte accessibility.

Titanium-based anodes coated with niobium and carbon have also been developed to improve charge-discharge rates and overall structural stability. The carbon coating plays a crucial role in enhancing CE and EE by optimizing electron transport and preventing material deterioration over extended cycling.

These advancements highlight the potential of composite electrodes in mitigating key limitations of AIRFBs, such as poor redox reversibility, high internal resistance, and electrode degradation [12].

4.2.2 Nanoparticle coatings

Surface modifications, such as nanoparticle coatings, have been investigated for their ability to make stability better and to suppress HER [2]. For example, one study presents a surface-modified carbon felt that makes the Fe anode more reversible for better performance in AIRFBs. Small nanoscale pores were added to the carbon fibers, which increases their surface area and makes them more hydrophilic. This change helps the Fe/Fe^{2+} redox reactions (see eq. 2) to work more efficiently and reversibly [13].

To further enhance charge transfer kinetics and mitigate dendrite formation during iron deposition, surface modifications and catalytic coatings have been studied. By modifying electrode surfaces with nanoparticle coatings and chemically treated carbon structures, researchers have been able to improve electron transfer rates and reduce polarization losses.

For example, thermal treatment of carbon felt electrodes at 600°C increases surface porosity and oxygen functional groups, leading to better wettability and reaction kinetics. Additionally, carbon nanotube (CNT) coatings on electrodes reduce charge transfer resistance, further enhancing electrochemical performance [1].

4.2.3 Anion exchange membranes

Parallel to electrode advancements, membrane technologies in AIRFBs have undergone refinements to reduce ion crossover and enhance selectivity. Anion exchange membranes (AEMs) have been explored as an alternative to conventional separators.

In AIRFBs utilizing $FeSO_4$ + TIPA as the electrolyte, AEMs control sulfate ion transport and minimize unwanted Fe^{3+} crossover. By selectively allowing sulfate ions (SO_4^{2-}) to migrate while restricting Fe^{3+} diffusion, these membranes help maintain charge balance and prevent capacity loss caused by iron accumulation on the wrong electrode. In systems based on $FeCl_2$, AEMs are often employed to facilitate chloride ion transport.

Recent developments in AEMs have focused on enhancing chemical stability and mechanical durability in acidic environments. Tested polymer-reinforced cross-linked structures are showing promising results in extending membrane longevity while maintaining high ion selectivity and minimal resistance [7].

4.2.4 Polyacrylonitrile-based graphite felt

Electrode materials impact directly charge transfer kinetics, electrochemical stability, and overall EE of AIRBF. One of the most widely used materials in AIRFBs is polyacrylonitrile-based graphite felt (PAN-GF) due to its high surface area and good electrical conductivity. However, untreated PAN-GF has limited wettability and relatively high charge transfer resistance, which can hinder reaction kinetics and contribute to increased polarization losses.

To overcome these challenges, thermal activation techniques have been employed to modify the surface properties of PAN-GF. By heating the material to 575°C in air, oxygen-containing groups like hydroxyl and carboxyl are added to the carbon surface. This modification improves electrode wettability. It allows for better electrolyte penetration and increased interaction with iron ions in solution.

Furthermore, the introduction of oxygen functionalities reduces charge transfer resistance and facilitates more efficient electron exchange between Fe^{2+} and the electrode surface. This occurs because oxygen-containing groups introduce localized polar sites on the carbon surface, enhancing electrostatic attraction between the electrode and Fe^{2+} ions. Additionally, these functional groups increase the surface energy of the electrode. The presence of these groups also modifies the electronic structure of the carbon material, creating additional active sites that lower the activation energy required for redox reactions.

The combination of thermally treated PAN-GF with $NaHSO_3$-modified electrolytes has shown remarkable improvements in battery performance. Experimental results demonstrated that the use of these electrodes led to higher current densities and lower overpotentials. Moreover, the structural integrity of PAN-GF remained stable over extended cycling, preventing electrode degradation [10].

4.2.5 Semi-solid electrode

Conventional porous electrodes suffer from passivation and structural degradation over prolonged cycling. Recent research has introduced a novel semi-solid electrode configuration. It consists of conductive solid particles suspended in an electrolyte, forming a dynamic and continuous conductive network. The effectiveness of the semi-solid electrode is primarily due to its ability to maintain high ionic conductivity while minimizing electrode passivation.

The semi-solid electrode is primarily made of multi-walled CNTs (MWCNTs) and activated carbon particles dispersed in an iron-based electrolyte. The inclusion of MWCNTs enhances electron transport by forming percolation pathways, reducing the internal resistance of the slurry electrode. The high surface area of activated carbon particles also provides large active sites for electrochemical reactions.

In conventional solid electrodes, this deposition process often leads to uneven growth and dendrite formation, which can weaken battery performance. In a semi-solid system, the mobility of conductive particles prevents localized accumulation, ensuring a more uniform and reversible deposition process. The continuous flow of electrolyte facilitates the efficient transport of iron species. Furthermore, the use of an external magnetic field has been shown to improve the connectivity of conductive particles.

5 Performance

5.1 Efficiency and energy density

AIRFBs' efficiency and energy density determine their practicality for large-scale energy storage applications. These metrics are primarily influenced by electrolyte composition, electrode design, and flow rate optimization.

Flow rate optimization directly impacts battery efficiency. Proper electrolyte circulation prevents concentration polarization and enhances mass transport, leading to higher CE and EE values. However, excessively high flow rates increase pumping energy consumption, which can offset efficiency gains. Studies indicate that maintaining an optimal electrolyte flow rate ensures effective redox species utilization, minimizes charge losses and improves overall battery performance.

Electrolyte formulation plays a key role in optimizing EE. An advancement in AIRFBs has been the introduction of a 2 M $FeSO_4$/EMIC-based electrolyte, which has demonstrated improved electrolyte solubility and iron deposition uniformity. The inclusion of EMIC strengthens sulfate-water interactions, enhancing $FeSO_4$ solubility and allowing higher electrolyte concentrations. Experimental results show that the $FeSO_4$/EMIC AIRFB achieved a competitive theoretical energy density of 32 Wh L^{-1} and CE of 70% at a current density of 20 mA cm^{-2}. Additionally, this system exhibited good cycle stability, operating for over 800 cycles without significant capacity decay [3].

Second example of advancements in AIRFB's EE is the Fe-TIPA/Fe-CN system, which achieved a high EE of 81% in a large-scale prototype system. The system maintained stability over 1831 cycles at 80 mA·cm^{-2}, with minimal capacity loss. The incorporation of the complexes significantly reduced ligand crossover and improved electrolyte stability. To further enhance long-term cycling stability, electrolyte formulation adjustments were made by incorporating supporting electrolytes such as KCl and Li_2SO_4. These modifications effectively mitigated volume changes and maintained conductivity balance, extending the system's lifespan to 2490 cycles. However, the EE slightly decreased to approximately 77%, likely due to increased ionic resistance and altered electrolyte transport properties. This trade-off highlights the balance between maximizing cycle life and maintaining high EE.

Another key factor influencing energy density is the concentration of active species in the electrolyte. While higher Fe^{2+} concentrations theoretically increase energy density, they can also lead to increased viscosity and mass transport limitations. Research has shown that a 0.4 M Fe-TIPA electrolyte exhibited twice the theoretical capacity compared to lower concentrations, but at the cost of slightly reduced EE. This trade-off highlights the need for balancing solubility, conductivity, and electrolyte stability to achieve optimal battery performance [4].

5.2 Durability

The long-term stability of AIRFBs is influenced by electrolyte composition, electrode material selection, and mitigation of unnecessary side reactions. Research has explored the use of ferrocene-based complexes, which improve redox potential and reversibility, and could further enhance battery lifespan. However, challenges such as dendrite formation and HER remain major obstacles to long-term durability [2].

The chemical reactions in RFBs primarily occur in the liquid phase. Avoiding solid-phase changes and allowing electrodes to remain inactive supports rapid charge-discharge cycling and extends the battery's service life. The system also maintains low operational temperatures due to the flow of electrolytes, which is good for durability [14].

5.3 Cost and scalability

One of the main advantages of AIRFBs compared to other battery systems is their lower cost. Sulfate-based iron electrolytes are a key to lower material expenses. Additionally, incorporating EMIC or other solubility enhancing additives improves electrolyte utilization, allowing for higher energy densities without increasing raw material costs. The ability to maintain high electrolyte solubility and stability also reduces the need for expensive membrane materials. Another cost-reducing factor is the high recyclability of iron-based systems. AIRFBs can utilize regenerated iron electrolytes, minimizing waste production and raw material consumption. This recyclability is a major advantage for long-term system sustainability.

Scalability remains another key strength, as modular designs enable flexible system expansion. Advanced manufacturing techniques such as roll-to-roll electrode production and optimized flow field designs have been shown to improve performance while lowering

fabrication expenses [15]. The inherent scalability of RFBs allows them to be adapted for various energy storage applications, with single cells combining into stacks of over 100 units connected through bipolar electrodes. Power output can be increased by expanding electrode area or linking multiple stacks in series or parallel configurations [14].

The economic feasibility of AIRFBs has also been demonstrated through industrial-scale prototype testing. A 25-cell stack with an active electrode area of 225 cm^2 achieved stable performance at 9.0 A, reaching CE of 97.6% and an overall EE of 81.3%. Cost modelling suggests that Fe-TIPA electrolyte could be produced at approximately $32.37/kWh, making it a highly cost-effective alternative to VRFBs, which currently exceed $300/kWh [4].

Despite the advantages, overall system costs could be further reduced through alternative synthesis methods, such as recycling spent electrolytes and employing 3D printing techniques for large-scale battery components. By leveraging these cost-saving strategies and scalability benefits, AIRFBs continue to emerge as a promising alternative to more expensive battery chemistries. Future technological advancements and large-scale production methods will further drive down costs, increasing their commercial viability [1].

6 Prospects

6.1 Challenges and possibilities

The future development of AIRFBs relies on further advancements in electrode engineering, electrolyte optimization, and cell design to enhance long-term stability and efficiency. For example, recent studies emphasize that improving Fe anode reversibility through carbon defect engineering can notably boost battery performance. Structural modifications like that optimize charge transfer, reduce polarization losses, and minimize side reactions [13].

Despite technological improvements, capacity decay, HER, and membrane selectivity limitations remain major obstacles. Addressing these issues requires novel electrolyte formulations**,** advanced electrode materials, and highly selective membrane structures. However, computational modelling and in-situ diagnostics are expected to provide insights into system optimization, helping to mitigate unwanted side reactions and improve efficiency [1].

6.2 Potential for commercialization

The successful commercialization of AIRFBs depends on overcoming key challenges related to cost, efficiency, and material durability. Large-scale manufacturing requires stable and efficient processes to ensure economic feasibility [2].

An example of AIRFB design today incorporates $FeSO_4$ electrolytes, a microporous membrane, and a glass fiber separator. This system achieving stable performance for over 800 cycles at a current density of 20 mA cm^{-2}. Cost analysis indicates that this AIRFB system could be implemented at approximately $50 per kWh, demonstrating great economic potential [3].

For ASAI-AIRFBs, commercialization efforts focus on electrolyte stability, membrane durability, and cost reduction. Researchers are actively exploring alternatives to expensive perfluorinated membranes and optimizing electrolyte formulations to suppress self-discharge and capacity decay, ensuring long-term viability for industrial applications [1].

As research continues, AIRFBs and ASAI-AIRFBs are becoming increasingly viable solutions for large-scale energy storage, grid balancing, and renewable energy integration.

6.3 Research gaps and recommendations

Despite major progress in AIRFBs, key challenges must be solved before they can be widely commercialized. While ligands such as Fe-TIPA and Fe-CN complexes have improved electrolyte solubility and stability, further studies are needed to optimize their long-term compatibility with existing battery materials and to minimize degradation over extended cycling [8,16].

The use of an external magnetic field represents a promising yet underexplored avenue in improving mass transfer efficiency in AIRFBs. Combining the methods, such as employing Fe-TIPA electrolyte while applying an external magnetic field, could further minimize polarization losses and increase overall system efficiency. However, additional research is required to evaluate the long-term stability of magnetic field-assisted electrolyte systems and their practical implementation in large-scale setups [11].

Another major research focus is the reduction of HER, which remains a critical source of energy loss in AIRFBs. Additives like $NaHSO_3$ have shown promise in suppressing HER and improving charge efficiency, but their effects on overall cycle stability and potential long-term electrolyte degradation require further investigation. Additionally, research into alternative electrolyte stabilizers could provide new strategies for suppressing unwanted side reactions [10].

The optimization of electrode materials is still a notable challenge. While thermally activated carbon felt and CNT coatings have improved charge transfer efficiency and durability, the long-term mechanical and electrochemical stability of these materials in continuous operation needs further evaluation [17]. Investigating new composite materials and surface modifications that boost electrode wettability and catalytic activity is crucial for enhancing performance and reducing internal resistance [13].

Membrane technology remains a critical challenge, as iron-ion crossover and degradation reduce efficiency and longevity. While conventional Nafion membranes offer high performance, their cost limits scalability. Alternative anion-exchange membranes (AEMs) and chemically modified ion-exchange membranes are being developed to improve charge selectivity while maintaining high ionic conductivity. However, further optimization is needed to balance ionic selectivity with low resistance, and the long-term chemical stability of next-generation membranes under real-world cycling conditions remains uncertain. Recent

studies suggest that AEMs could provide a viable alternative to traditional cation-exchange membranes like Nafion, but their commercial feasibility is still under evaluation.

Compared to conventional electrodes, semi-solid electrodes offer a unique advantage by eliminating the fixed structure limitations of solid electrodes. Unlike nanoparticle coatings, which enhance charge transfer by modifying surface properties, semi-solid electrodes actively prevent electrode passivation by maintaining continuous electrolyte-electrode interaction. However, their long-term mechanical stability remains a concern, particularly in high-current-density applications. Further research is required to determine whether semi-solid electrodes can be effectively integrated with existing electrode materials, such as PAN-GF, to combine the benefits of both technologies [11].

Beyond material advancements, system-level improvements such as optimized flow field designs, stack architecture refinements, and scalable manufacturing techniques are needed to make AIRFBs more competitive with existing commercial battery systems. While laboratory-scale studies have demonstrated high energy density, large-scale implementation still faces economic and engineering challenges [15].

Future research should also explore computational modelling and in-situ diagnostic tools to predict long-term degradation mechanisms and optimize cell performance in real time. These techniques could accelerate the development of more robust battery designs and improve predictive maintenance strategies [7].

By addressing these research gaps, AIRFB technology can continue evolving toward cost-effective, durable, and scalable energy storage solutions suitable for large-scale renewable energy integration.

7 Conclusions

AIRFBs have emerged as a promising solution for large-scale energy storage, combining cost-effectiveness, safety, and scalability. Their use of abundant iron resources and the ability to decouple power output from energy capacity make them a viable alternative to conventional battery technologies. Recent advancements in electrolyte chemistry, electrode engineering, and membrane design have significantly improved system performance, enhancing efficiency, durability, and commercial feasibility [1,2].

The introduction of Fe-TIPA and Fe-CN complexes has notably enhanced electrolyte stability, reducing ligand crossover and increasing EE [4]. Additionally, $NaHSO_3$-based additives have improved iron plating-stripping kinetics, leading to higher CE and longer cycle life [10]. Advancements in electrode surface engineering, such as CNT coatings and thermally treated graphite felt, have further optimized charge transfer and minimized polarization losses [13].

Improvements in membrane technology, including AEMs and chemically modified separators, have reduced iron-ion crossover and extended operational stability [6]. Additionally, flow field design refinements, such as FO and FT configurations, have enhanced mass transfer efficiency, contributing to higher overall performance [18].

Despite these advancements, key challenges remain before AIRFBs can achieve widespread commercialization. HER, iron-ion crossover, and membrane degradation continue to limit system efficiency and longevity. Future research should focus on alternative membrane materials, optimized electrolyte additives, and novel electrode architectures to address these limitations [15,16].

Economic feasibility remains a decisive factor for application of AIRFBs. The low-cost nature of sulfate-based iron electrolytes, high recyclability, and potential for large-scale manufacturing support the economic viability of this technology [15]. Ongoing innovations in automated production techniques, computational modelling, and large-scale prototype validation will be essential in advancing AIRFBs toward commercial deployment [3,17].

This study has provided a comprehensive review of AIRFB principles, recent technological advancements, and prospects. With continued research and development, AIRFBs have the potential to become a key player in grid-scale energy storage, supporting the integration of renewable energy sources and contributing to a more sustainable energy future.

8 References

[1] S. Zhang, S. Gao, Y. Zhang, Y. Song, I. R. Gentle, L. Wang, B. Luo, All-soluble all-iron aqueous redox flow batteries: Towards sustainable energy storage, Energy Storage Materials, Vol. 75, (2025) 104004. https://doi.org/10.1016/j.ensm.2025.104004 (accessed February 7, 2025).

[2] B. S. Jayathilake, E. J. Plichta, M. A. Hendrickson, S. R. Narayanan, Improvements to the Coulombic Efficiency of the Iron Electrode for an All-Iron Redox-Flow Battery, J. Electrochem. Soc. 165 (2018) A1630–A1635. https://doi.org/10.1149/2.0451809jes (accessed February 4, 2025).

[3] H. Zhang, C. Sun, A Low-Cost Sulfate-Based All-Iron Redox Flow Battery, J. Power Sources 411 (2019) 1–11. https://doi.org/10.1016/j.jpowsour.2021.230457 (accessed January 17, 2025).

[4] J. Yang, W. Wei, C. Zhou, H. Yan, H. Che, L. Hao, X. Tan, A. W. Robertson, T. S. Wu, Y. L. Soo, A. Tang, Z. Sun, High-Stable All-Iron Redox Flow Battery with Innovative Anolyte Based on Steric Hindrance Regulation, Angew. Chem. Int. Ed. (2024). https://doi.org/10.1002/anie.202414452 (accessed February 11, 2025).

[5] L. Ye, et al., Vanadium Redox Flow Battery: Review and Perspective of 3D Electrodes, ACS Nano 18 (2024) 18852–18869. https://doi.org/10.1021/acsnano.4c06675 (accessed February 15, 2025).

[6] Y. Zhao, H. Zhang, C. Sun, A Strategy for Lowering Cross-Contamination of Aqueous Redox Flow Batteries Using Metal-Ligand Complexes as Redox Couple, J. Power Sources 399 (2018) 1–7. https://doi.org/10.1016/j.jpowsour.2021.230810 (accessed February 19, 2025).

[7] M. Skyllas-Kazacos, M. Rychcik, R. G. Robins, A. G. Fane, M. A. Green, Progresses and Perspectives of All-Iron Aqueous Redox Flow Batteries, Adv. Funct. Mater. 13 (2003) 263–270. https://doi.org/10.1002/adfm.202302077 (accessed February 4, 2025).

[8] A. Z. Weber, et al., Redox Flow Batteries: A Review, J. Appl. Electrochem. (2011). https://doi.org/10.1007/s10800-011-0348-2 (accessed March 1, 2025).

[9] B. Liu, et al., Recent Advances in Redox Flow Batteries Employing Metal Coordination Complexes, J. Energy Chem. (2023). https://doi.org/10.1007/s41918-023-00205-6 (accessed February 27, 2025).

[10] A. Concheso, et al., $NaHSO_3$ as a Key Component in Developing Enhanced Performance Electrolytes for All-Iron, Battery Energy (2025). https://doi.org/10.1002/bte2.20240059 (accessed March 2, 2025).

[11] H. Li, et al., Exploring the Flow and Mass Transfer Characteristics of All-Iron Semi-Solid Redox Flow Battery, SSRN (2024). https://doi.org/10.2139/ssrn.5044452 (accessed February 28, 2025).

[12] W. J. Moura, et al., Development of New Cathode Materials for All-Iron Redox Flow Batteries Using Hard Carbon-Based Composites Containing Niobium Pentoxide, J. Electroanal. Chem. 973 (2024) 118694. https://doi.org/10.1016/j.jelechem.2024.118694 (accessed March 11, 2025).

[13] Y. Zhao, L. Zhang, H. Zhang, C. Sun, Surface Engineered Carbon Felt Toward Highly Reversible Fe Anode for All-Iron Flow Batteries, Chem. Eng. J. 360 (2019) 1216–1224. https://doi.org/10.1016/j.cej.2024.150592 (accessed February 22, 2025).

[14] H. Zhang, C. Sun, Cost-Effective Iron-Based Aqueous Redox Flow Batteries for Large-Scale Energy Storage Application: A Review, J. Power Sources 390 (2018) 136–153. https://doi.org/10.1016/j.jpowsour.2020.229445 (accessed January 26, 2025).

[15] Y. Zhang, X. Xiang, H. Zhang, C. Sun, Low-Cost All-Iron Flow Battery with High Performance Towards Long-Duration Energy Storage, J. Energy Storage 32 (2020) 101859. https://doi.org/10.1016/j.jechem.2022.06.041 (accessed January 11, 2025).

[16] J. Sun, et al., Redox Flow Batteries and Their Stack-Scale Flow Fields, Carbon Neutrality (2023). https://doi.org/10.1007/s43979-023-00072-6 (accessed February 22, 2025).

[17] X. Wu, Y. Zhang, H. Zhang, C. Sun, Study on the Treatment of Carbon Black for Slurry Electrodes of All-Iron Redox Flow Batteries, Electrochim. Acta 299 (2019) 772–779. https://doi.org/10.1016/j.electacta.2024.145393 (accessed March 9, 2025).

[18] J. J. Bailey, et al., All-Iron Redox Flow Battery in Flow-Through and Flow-Over Set-Ups: The Critical Role of Cell Configuration, RSC Adv. (2024). https://doi.org/10.1039/D4YA00179F (accessed February 28, 2025).