

CHAPTER 6

REDOX FLOW BATTERIES

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Abstract

Redox flow batteries (RFBs) offer a readily scalable format for grid scale energy storage. This unique class of batteries is composed of energy-storing electrolytes, which are pumped through a power-generating electrochemical cell and into large storage tanks. Despite this common underlying design, a myriad of different electrolyte chemistries and electrochemical cell designs have been investigated, some of which have been successfully commercialized. This chapter reviews state-of-the-art flow battery technologies, along with their potential applications, key limitations, and future growth opportunities.

Key Terms

anolyte, catholyte, flow battery, membrane, redox flow battery (RFB)

1. Introduction

Redox flow batteries (RFBs) are a class of batteries well-suited to the demands of grid scale energy storage [1]. As their name suggests, RFBs flow redox-active electrolytes from large storage tanks through an electrochemical cell where power is generated [2, 3]. The electrolytes are specifically designed such that they can be electrochemically reduced (accept electrons) or oxidized (provide electrons) [4]. One tank of the flow battery houses the cathode (catholyte or posolyte), while the other tank houses the anode (anolyte or negolyte). Figure 1 is a schematic of a typical, single cell flow battery used for research and development. Here the catholyte (green) is housed in the tank on the left, while the anolyte (blue) is housed in the tank on the right. These electrolytes are flowed through the serpentine flow field of the electrochemical cell at the center of the figure. The flow field is commonly made from carbon and serves as the current collector as the electrolytes are oxidized and reduced. Adjacent to the flow fields reside porous carbon electrodes, maximizing the contact area with the liquid electrolyte. Between the porous carbon electrodes resides a separator. Typically, the separator is an ion-selective membrane such as Nafion [5, 6] Such membranes enable transport of inert ions necessary to charge-balance the electrochemical reactions, while preventing electronic shorting of the opposing carbon electrodes and physical mixing of anolyte and catholyte.

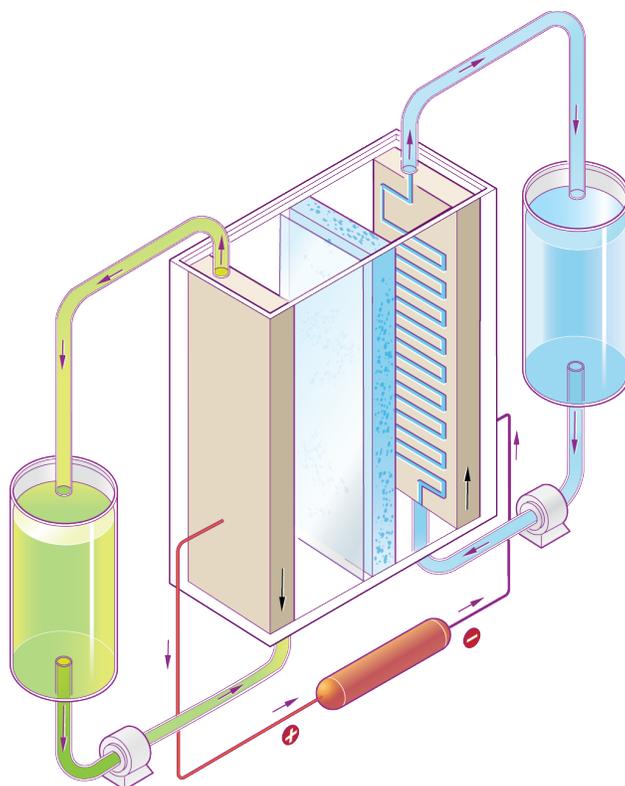
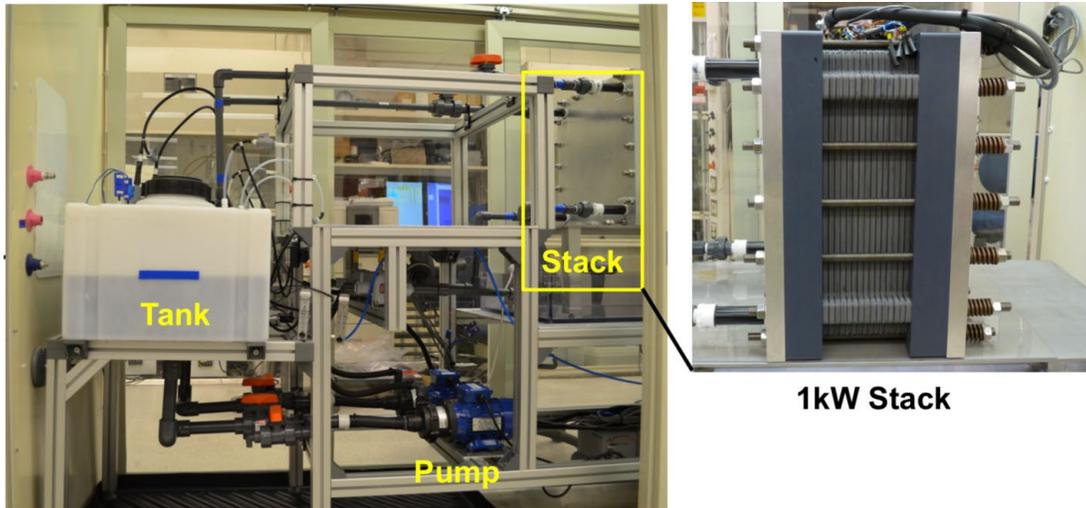


Figure 1. Schematic of a single cell RFB, depicting electrolyte flowing from storage tanks through the serpentine flow field within the electrochemical cell

To generate higher power necessary for practical applications, many flow cells are strung together. Figure 2 shows a photograph of a 1 kW/1 kWh vanadium RFB test bed used at Pacific Northwest National Laboratory (PNNL) [7]. An enlarged view is provided of the 1 kW cell stack, consisting of 15 cells strung together between the thick steel plates. Here, the 15 cell electrodes are placed in series, increasing the stack voltage by a factor of 15, while the anolyte and catholyte are pumped in parallel through each cell individually.



1kW / 1kWh VRFB System

Figure 2. Photograph of vanadium RFB (VRFB) test bed developed at Pacific Northwest National Laboratory for RFB evaluation. A zoomed in image of the electrochemical cell stack is provided at right.

Flow batteries are particularly attractive for their ability to decouple energy and power. The specific choice of catholyte and anolyte chemistry will dictate the voltage of an individual cell and the energy density of the system. Therefore, the overall energy of a flow battery may be controlled by varying the volume of electrolyte. On the other hand, the power can be effectively manipulated through design of the electrochemical cell. Thus, a high energy flow battery aimed at long duration discharge might couple large volumes of electrolyte with a modestly sized electrochemical cell, whereas a high power, short duration flow battery might only require smaller volumes of electrolyte but leverage a significantly larger electrochemical cell.

Flow batteries offer several potential safety features compared to regular, nonflowing batteries. Unlike traditional batteries, the bulk of the anolyte and catholyte are spatially separated from each other in large tanks. Thus, it is considerably harder to release all the stored energy under nonstandard or emergency conditions. Even if the electrochemical cell were to rupture, valves could be closed and the anolyte and catholyte would remain separated. Moreover, most flow batteries commercialized today use aqueous-based electrolytes, rendering them nonflammable. Depending on the exact electrolyte chemistry employed, flow batteries can also be non-toxic and non-corrosive.

2. State of Current Technology

2.1. Current Implementation

2.1.1. Electrolyte Chemistries

A variety of different electrolyte chemistries exist in the flow battery market. Currently commercialized electrolytes almost exclusively use aqueous (water-based) electrolytes. The exact electrolyte formulation largely dictates the cell voltage, energy density, and operating temperature range of the RFB. The following discussion outlines several classes of electrolyte chemistries that have been commercially evaluated. This discussion is not meant to be an exhaustive list. As of the

time of writing, over 100 different companies are developing RFBs, each with their own electrolyte formulations.

2.1.1.1. Iron-Chromium

Originally invented by NASA in the late 1970s, the iron chromium (Fe-Cr) system was the first RFB electrolyte system developed [8, 9]. It consists of an $\text{Fe}^{2+/3+}$ catholyte coupled with a $\text{Cr}^{2+/3+}$ anolyte in an acidic aqueous electrolyte. On discharging, the following redox reactions occur:



A cell voltage of 1.2 V is typical, with metal ions dissolved at ~ 1 M concentrations. In general, the $\text{Cr}^{2+/3+}$ redox reactions are sluggish compared to other chemistries, requiring use of a catalyst [3]. Moreover, the dissimilar catholyte and anolyte mean that transport of catholyte to anolyte, and vice versa, leads to permanent loss in battery capacity. Nevertheless, NASA has demonstrated this chemistry on a 1kW/13kWh scale, and even larger scale by others, as described later in this chapter.

2.1.1.2. All-Vanadium

Currently, the most widely commercialized RFBs all use vanadium-based electrolytes. The basis for this chemistry was first developed by Skyllas-Kazacos and coworkers in 1984 [10, 11]. Here, the anolyte and catholyte both consist of aqueous acidic solutions of vanadium. Using the same electrolyte for anolyte and catholyte is beneficial in that if transport of one to another occurs it does not permanently damage RFB capacity. Upon discharge, the following redox reactions occur in a vanadium RFB:



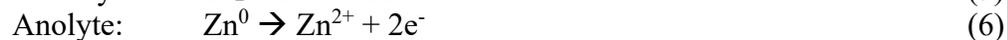
Note that the V^{5+} and V^{4+} are typically oxo-complexes such as VO_2^+ and VO^{2+} , respectively. Vanadium concentrations are typically on the order of 1-3 M. Coupled with a nominal cell voltage of 1.6 V, an energy density of around 20 Wh/L is observed. The exact composition of the electrolyte is the focus of much research, with various groups experimenting with different acid types, complexing agents, and vanadium purities, leading to improvements in operating temperature and energy density, among others [2, 12, 13].

2.1.1.3. All-Iron

To decrease the cost of RFBs, researchers have developed all-iron systems. There are several variations of this chemistry, though fundamentally all employ the $\text{Fe}^{2+/3+}$ couple in the anolyte. The catholyte may contain the $\text{Fe}^{2+/0}$ couple or the $\text{Fe}^{2+/3+}$ complexed with different ligands from those in the anolyte. Use of the $\text{Fe}^{2+/0}$ couple requires electroplating solid Fe metal on the anode while charging. Sometimes the use of a solid electrode in an RFB is referred to as a “hybrid redox flow battery.” The catholyte chemistry can be fairly sophisticated, with various Fe-complexes (e.g., $\text{Fe}(\text{CN})_6^{3-/4-}$) tailored to enhance RFB cell voltage and stability [14-16]. The exact cell voltage depends on the chemistry employed but is typically in the 0.75-1.2 V range.

2.1.1.4. Zinc-Bromine

Perhaps the most complicated of all the commercialized RFB electrolyte chemistries is Zinc-Bromine (Zn-Br). Here, metallic zinc is plated and stripped on the anode, while liquid bromine is evolved and reduced from the cathode. Like the all-Fe RFB, the Zinc-Bromine RFB can be considered a “hybrid flow battery.” Upon discharge of the RFB, the following redox reactions occur:



The relatively high theoretical cell voltage of 1.82 V, coupled with the high electrolyte concentrations, enable an energy density of 60-70 Wh/L. This chemistry is more complicated than others in that multiple phase-change reactions occur. Whereas with most of the previous electrolyte chemistries all reagents remain in the liquid phase, here zinc is electroplated out as a solid and bromine is evolved into the liquid phase. Advanced complexing agents are added to the electrolytes to stabilize Br- and Zn-containing species and minimize the Br₂ vapor pressure and Zn dendritic growth [17, 18, 19].

2.1.2. Separators

The primary role of the membrane separator is to allow the flow of electrolyte between the positive and negative compartments for charge balance, while preventing the transport of electroactive species, which leads to capacity decay. Other key attributes of the membrane are high oxidative/reductive stability, flexible mechanical properties, and low cost. The membrane separator is a critical component to flow battery performance, durability, and cost. However, a membrane that satisfies all the mentioned requirements does not exist, thus current research efforts are focused on a variety of membrane composition and morphology to optimize flow battery performance.

There are two broad categories of flow battery membranes: 1) ion exchange membranes: dense film with ionic moieties that are tethered to a hydrocarbon or perfluorinated backbone, which instills hydrophilic character, and 2) porous membranes with nonionic polymer backbone and engineered pore size/density. Both types of membranes have positive attributes, but also have properties that need to be further improved, which will be discussed in Section 2.3.2 Membranes.

There are two types of ion exchange membranes that are differentiated by the type of bound charge in the polymer backbone. The bound charges in the polymers develop a Donnan potential, which determines the ion selectivity of the membrane.

Cation exchange membranes (CEM) have fixed negative charges with a negative Donnan potential that predominantly allows cation mobility through the membrane. The opposite is found in anion exchange membranes [20, 21]. The attached negative charge is typically a sulfonate moiety, due its stability and high ion dissociation values. However, carboxylate and phosphonate groups have also been investigated. The state-of-the-art of cation exchange membranes are perfluorinated sulfonic acid (PFSA) such as Nafion (Chemours), Aciplex (Asahi) or Flemion (AGC). These types of membranes are industrially employed in the chloro-alkali process and used in large demonstration-size acidic vanadium and Fe-Cr flow batteries due to low proton resistance and superior chemical durability. The primary downside to PFSA membranes is high cost, which accounts for up to 30-40% of the stack hardware [22, 23]. Sulfonated hydrocarbon polymers are being developed as low cost alternatives to PFSA due to inexpensive chemical feedstock and

benchmark preparation [24]. The wide diversity of hydrocarbon backbones—poly(arylene ether ketone), poly(styrene), poly(phenylene oxide), poly(phenylene), etc.—and precise control of ion content levels allow for chemically engineered membranes with low proton resistance and high ion transport selectivity. The key deficiency, and what R&D efforts seek to improve, is the oxidative durability of sulfonated hydrocarbon membranes compared to PFSA type material.

Anion exchange membranes (AEMs) contain fixed positive charges and have positive Donnan potentials. The positive charge is typically a variant of an ammonium moiety, however imidazolium, phosphonium and guanidinium are also being developed. Unlike CEMs, there is no large end user (such as with the chloro-alkali process) that employs AEMs, which have primary use in membrane-based water treatment [25]. However, AEMs have been employed in vanadium RFB by Kashim-Kita Electric Power Corporation and Sumitomo Electric Industries in a 200kW x 4 h demonstration system [26, 27]. The advantage of AEMs in vanadium RFBs is lower vanadium permeability through the membrane due to the Donnan exclusion effect, however, concerns over lower proton conduction and long-term stability are valid [28]. Other opportunities for AEMs are in neutral and high pH environments that are being developed in aqueous organic flow batteries [29, 30]. Unlike CEMs, there is no state-of-the-art material (such as PFSA) in AEMs because of three different durability concerns in alkaline media that current R&D efforts seek to improve: 1) backbone stability 2) positive moiety stability, and 3) oxidative stability [31, 32].

2.1.3. Integration with the Electric Grid

RFBs come in a range of sizes, from small 1 kWh residential systems, to multi-MWh industrial systems. While significant variability in form-factor and enclosure design exists at the smaller scale, large industrial systems are usually packaged in shipping containers. These containers typically house all RFB systems—electrolyte storage tanks, pumps, electrochemical cell stack—along with power electronics necessary to connect the DC power of the flow battery to the AC power of the residential, commercial, or industrial-level electric grid. Details on power electronics can be found in Chapter 13: Power Conversion Systems.

2.1.4. Major Players

Of the more-than 100 RFB companies currently working in the industry, most are start-ups developing new RFB technologies, particularly electrolytes. Large established corporations such as Sumitomo Electric Industries, a large Japanese multinational corporation, and Dalian Rongke Power Co. dominate large utility scale projects. Other manufacturers include UniEnergy Technologies, Primus Power, StorEn, Redflow, RedT Energy, and Avalon, among others. Many large industrial companies conduct research into RFBs and license their technologies to startups, such as the relationship with United Technologies and the startup Vionx. Other large corporations, such as Lockheed Martin, have also directly entered the RFB business, recognizing that energy storage will become a ubiquitous part of the national electrical grid and a strategic asset in defense applications.

2.1.5. Deployment Examples

Over the past decade, many different RFB systems have been deployed throughout the world. While their total capacity pales in comparison to overall electrical power consumption, these RFB installations provide pertinent use-case information and demonstrate how RFBs can successfully be integrated with the electric grid.

At the small-to-medium scale, Australian company RedFlow has achieved success deploying their Zn-Br based systems on residential (~20-60 kWh) to commercial and industrial customers (~100 kWh). When coupled with solar power, these systems have enabled customers to operate off-grid. At the commercial level, these systems provide flexibility in power time of use and allow companies to keep the lights on during blackouts [33].

RFBs have been successfully coupled with industrial agriculture in the Central Valley of California. In 2014, EnerVault Corp. successfully demonstrated a 250kW/1MWh Fe-Cr RFB that was charged by a 150 kW PV system or the grid and used to run a ground water irrigation pump. An aerial photo of this installation is provided in Figure 3. EnerVault leveraged several proprietary designs to improve RFB technology and successfully deploy this Fe-Cr RFB [34]. While the project was a technical success, EnerVault filed for restructuring in 2015.



Figure 3. Photograph of EnerVault Corp.'s 250kW/1MWh Fe-Cr RFB in Turlock, California. Electrolyte is held in the four tanks in the lower right [34].

UniEnergy Technologies has integrated several RFBs into the electrical grids across Washington State. A 1MW/4MWh system was installed in Pullman, WA, using both grid-tied and islanding operations. A 2MW/8MWh vanadium RFB installed in Everett, WA was successful in shifting peak demand, improving electrical power distribution, and enhancing grid voltage control [35].

The largest RFB built to date resides in Dalian, China, where Rongke Power is constructing a 200MW/800MWh vanadium RFB, with completion scheduled in 2020. The RFB is targeted at peak-shaving applications, easing grid strain under extreme weather conditions. Despite the RFB large capacity, this represents about 8% of total projected electrical grid load in Dalian [36].

2.2. Challenges

The main challenges facing RFBs are related to cost and energy density. Decreasing the cost of electrolyte and membrane materials would go a long way toward increasing RFBs' competitiveness against other energy storage technologies on a \$/kWh scale. However, the active ingredient in many RFBs, vanadium, is costly, as are the ion exchange membranes used as

separators (Nafion). Additionally, these separators often provide less than ideal electrochemical performance, decreasing battery performance over time.

While flammability is often not a hazard for RFBs, as most electrolytes are aqueous-based, many of the electrolytes are toxic and corrosive. Coupled with RFBs' low energy density, this implies a large volume of hazardous material is required to store energy. This hazardous material may limit installation sites and require special permitting.

Last, some RFB chemistries are sensitive to extreme temperatures (e.g., $>40^{\circ}\text{C}$, $<-5^{\circ}\text{C}$), limiting the geographical locations where they may operate without expensive, energy-robbing temperature control systems [12].

2.3. Opportunities/Emerging Technologies

2.3.1. Electrolyte Chemistries

2.3.1.1. Aqueous Soluble Organics

To decrease the electrolyte cost, many researchers have focused on developing aqueous-soluble organic species capable of storing electrical charge. These so-called aqueous soluble organics are derived from inexpensive organic materials readily produced in the petrochemical industry, or even found in nature. Modest or even no modification is necessary to yield redox-active species useful in an RFB. While many such chemistries display low cell voltages and energy densities, they can be exceedingly inexpensive and have very long cycle lives. In the research literature, many potential chemistries have been shown to be successful and many startups have formed around these successes [37, 38].

2.3.1.2. Nonaqueous Electrolytes

The cell voltages of aqueous RFBs are limited by the voltage stability window of water. Various technologies and aqueous electrolyte chemistries may stretch this voltage slightly beyond 1.5 V but fail to reach voltages typical of Li-ion batteries (e.g., 3-4 V). The use of nonaqueous electrolytes, however, removes this limit and provides considerable freedom to choose more energetic chemistries. Voltages in excess of 2.5 V and redox-active species solubilities $>1\text{ M}$ are achievable and might allow these technologies to be viable if long term stability can be proven [39, 40]. While nonaqueous electrolytes promise more energy-dense RFBs, membranes tailored for specific nonaqueous electrolytes will need to be developed to enable their long-term success [41]. Moreover, electrolytes will need to be carefully chosen to satisfy safety requirements.

2.3.2. Membranes

To improve the transport selectivity of ion exchange membranes, CEM and AEM can be combined either by spray coating or electro spraying to form a bipolar membrane [42]. This type of asymmetric membrane improves flow battery performance by reducing capacity fade and excessive electro osmosis, however R&D will need to focus on improving ion conductivity/membrane interface, durability, and cost of production [43, 44].

Porous membranes are films with specific pore size and pore density and are commonly used in lead acid, zinc and Li-ion batteries. Well known examples of porous, commercially available membranes are Celgard and Daramic. These films are composed of uncharged polymers such as poly(ethylene) or poly(propylene) that are either extruded then stretched to form pores (dry

process) or the polyolefin resin is mixed with a hydrocarbon liquid; the melt is extruded, oriented, and the liquid phase extracted (wet process). The advantage of these materials is their relatively low costs, compared to PFSA and their durability in electrochemical environments. The disadvantage of these materials in flow batteries, however, is transport selectivity, because the permeation of species through the membrane is regulated only by size exclusion. R&D in this area seeks to control pore size/density synthetically; recent review papers provide more details [45, 46].

3. Concluding Remarks

RFBs offer a unique, adaptable solution to meet a wide range of energy storage requirements of the future. By decoupling energy and power, RFBs can be designed for a range of energy storage and power demands. The near limitless possibilities for electrolyte chemistries further play to RFBs advantage, allowing them to stay at the cutting edge while other more traditional chemistries (e.g. Pb-acid) rise and fall. Moreover, several key features of RFBs can make them significantly safer than other electrochemical energy storage technologies. In sum, the push toward longer duration energy storage, firming up wind and solar resources, coupled with the drive for safer, less-flammable energy has put flow batteries in a unique position to increase market share in the near future.



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Harry D. Pratt III is a distinguished technologist in the Advanced Power Sources R&D group at Sandia National Laboratories. Since 2011, Harry has assembled, tested, and optimized hundreds of flow batteries across a wide variety of chemistries.



Travis M. Anderson is a distinguished staff member in Sandia National Laboratories' Advanced Power Sources Research and Development group. Travis obtained his PhD in inorganic chemistry from Emory University in 2002. He has over 10 years' experience in advanced energy materials research and development. His research interests focus around the synthesis and characterization of redox-active coordination complexes, flow batteries, and thermal battery aging.

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