

A Review on Energy Storage System for Redox Flow Batteries

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Abstract: Redox flow batteries are suitable for modular and flexible energy storage systems for different applications of power Storage. In recent Decades, the energy resources available have been rapidly and continuously depleted and could lead to serious global energy crises. Researchers focus on developing new and renewable energy resources to meet the growing fuel demand and reduce greenhouse gases emitted from engineering to use redox- flow batteries, including recent advances on new active redox materials, cell designs and systems. There is also increasing research effort to replace hybrid and electrical alternative fossil-fuel-based vehicles. The best combination of power, cost, and versatility are electrochemical energy storage systems and redox battery flow systems that are currently the most important in this area. In this work the various flow battery redox systems and their hybrid alternatives are provided with a panoramic overview. Documented and critically discussed related published work. A systematic analysis of the technologies available is carried out in terms of both technological and environmental aspects. A host of other study opportunities and a number of flow battery limitations are addressed as well as technological challenges. The flow battery technologies examined have gained the most attention and promise for all redox flow batteries in various pre-commercials to stationary applications up to now, while new advances in hybrid redox fuel cells promise to lead for future mechanical or electrically re- powered applications. Although relatively new, the technology has the potential to improve dramatically by lowering material costs, improving performance and significantly reducing the overall device costs.

Keywords: Batteries; energy storage systems; grid integration; redox flow batteries; renewable integration.

Introduction

Energy storage systems are becoming increasingly involved in a wide range of applications in the electricity industry, from increasing grid reliability and stability to reducing renewable sources such as wind and solar, and providing backup power to areas with a limited grid access or in off-grid applications [1]. The electrical storage (EES) is a set of technologies that have been developed since the 1970s to support a growing fleet of nuclear power plants and different battery technologies beginning to deploy in a number of different EES applications [2]. The PHP and compressed air (CAES) systems are the technology used for storage of electrical energy [3].

Whereas the current fleet of worldwide storage is predominantly PHP systems, the varying needs of distributed energy storage are increasingly met by other EES technologies including the electrical chemical energy storage [4]. After the first oil crisis in the 1970's, major basic work and planned large scale electrochemical energy storage deployment took place. This first work led to the demonstration of large scale energy storage batteries using lead-acid batteries and the advancement of new technology, including redox flow batteries and sodium- sulfur batteries (RFBs) [5]. These early development efforts continued with limited company implementations in the late 1980s. Recently, the distribution of EES was attracted by growing penetration of wind and solar power systems through substantial new R&D investments in flow battery technology [6].

RFBs, with fluid electrolytes which are separate from the electrochemical cells, which allow for the energy and power secession, are unique among electrochemical energy storage technology. As a result of this unusual environment, the Flow Battery System (FBS) provides some essential advantages with regard to traditional batteries, where the reactants as well as the cell components are packed together [7]. The most obvious advantage of an FBS is that its design versatility is focused on two main modular components (i.e. stack and reacting tanks) that allow for goods that are power to energy based on a wide variety of power or energy ratios [8]. This unique battery architecture also has the benefit of having the active reactants in separate tanks, which is of particular significance for large scale EEES applications [9]. Flow batteries are more secure than regular batteries. Floating electrolytes furthermore contribute to superior thermal regulation and cell to cell balance, thereby enhancing the safety of batteries. Since reactants are also available easily, it is easy to calculate the charge status (SOC) accurately without inserting a destructive SOC detector into the individual cells [10].

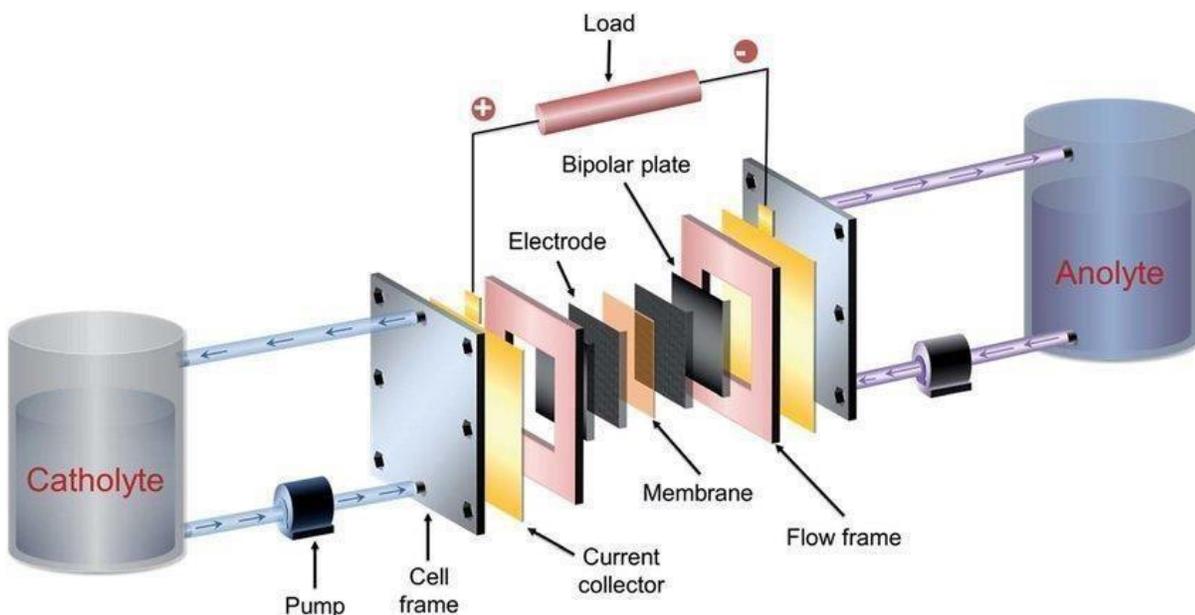


Figure 1: Schematic diagram of Redox flow battery with components

The flow of batteries also has some less visible advantages. The traditional batteries have at least one solid active ingredient that limits electric conductivity and the amount of current that can flow through them and the amount of active ingredient that can be contained in each electrode [11]. Since active materials are stored in tanks in

flow batteries, flow batteries can be extremely high in power without the use of thick electrodes. In theory, a flow battery can provide high power and high energy in one unit, whereas the design of conventional batteries often involves a compromise between high energy (thin electrodes are required) and high power (thick electrode is needed) (which requires thick electrodes) [12]. Moreover, since a traditional battery has a repetitive load or unload cycle, electrode material expands and contracts, resulting in time degradations and significantly limiting the cyclical lifetimes of solid state electrode batteries; this applies in particular to batteries with a relatively thick electrode, which must often be deep cycles, long SOC cycles [13]. During charge or discharge cycles, flow battery electrodes are not required because changes occur in active materials that are not addressed by liquid solutions [14]. The cycle life of FBS cells thus does not rely necessarily on the discharging depth and the use of relatively costly active material can be high, without affecting the cyclical life given that the battery and the individual cells run in their permitted temperature and voltage range. Flow batteries can therefore be designed to produce power over many hours without detrimental impacts on flow battery stack cycle life or energy density [15].

This specific system architecture makes the technology fully modular and scalable for a wide range of stationary EES applications and especially appealing for applications with long drive times. In renewable energy integration, for instance, a reserve capacity of 10h is required if a generation plant with a 10 MW high demand of 10 hours is to be adequately supported. In the case of traditional generation, the current spinning supplies, including coal or gas power plants, can easily accommodate this. If traditional batteries, for example plumbing acid or lithium-ion batteries, are to empty this reserve, then a 100 MWh energy storage capacity is needed. This will involve a very large number of battery cells because the thickness of the electrodes restricts the energy capacity of an individual cell [15-18]. The cell which can deliver nominal power over a multiple hour discharge cycle, particularly over 1000 s of low discharge cycles, is inappropriate for most solid state battery electrodes. In order to handle a 10-hour discharge, one must use several cells, leading to many sets of inactive cell materials (i.e., separators, electrodes, current collectors). For this purpose, traditional batteries have started to operate in EES applications requiring relatively short discharge times, for example in applications of power quality[17].

Table 1 highlights the major advantages and drawbacks of traditional rechargeable batteries and flow batteries. Conventional secondary batteries have higher energy densities and a simpler device than flow batteries. However in order to reduce the overheating and internal short circuit potential, comprehensive security electronics as well as control systems are required for any large EES systems [18]. The type of EES equipment depends on application requirements including response time and length of the discharge and these two primary EES requirements for different main types of EES technologies are considered on a qualitative basis in Table 1. While the main benefit of the RFB system over a traditional system is that it is used for energy-intensive applications, it can be configured with the correct system design and control to react very rapidly. In summary, even though RFBs typically have lower energy densities (due to limited solubility of the active redox species in the electrolytes, and relatively low cell voltages in the case of aqueous electrolytes), these systems do not have the energy capacity limitations of lead acid and lithium ion batteries. Indeed, RFB's become cheaper when power (kilowatt) and energy equilibrium (kilowatt-hour) are needed, as higher cell sizes result in less contribution from inactive components, including

plastic frames and separator materials [19]. In other words, RFBs are ideally suited for large scale EES applications that require thousands of deep discharge cycles, particularly where multi- hour loading and discharge times consist of average cycles [20].

Full Flow Systems of the two mature chemicals are the all vanadium redox (VRB) and iron chrome batteries, between the full flow systems (FeCr). All vanadium and FeCr are shown in the basic configurations in Fig. 2. FeCr was developed in the United States. The University of New South Wales announced in the 1980s that the national aeronautics and space management (NASA) was in the 1970s, with the first efficient vanadium redox battery flow device. At first, NASA was successful in developing FeCr in the kilowatt region, but further progress was limited by the lack of electrochemical reversibility for chromium, cross migration, the loss of hydrogen power and the need to improve the overall performance of the device for electrocatalysts. Research on this technology started to grow further in Japan in the 80s and continues to develop for various newcompanies.

Application Requirements	Rated Power Run Time (top row) and Desired Response Time (bottom row)		
	Seconds-to-Minutes	Minutes-to-Hours	Hours-to-Days
EES Technology type	Fast (≤ 10 sec.)	Med. (≤ 10 min.)	Slow (≤ 1 h)
Flow Battery (e.g., VRB) Vanadium Redox Battery	With proper system design & controls ¹		
Hybrid-Flow Battery ² (e.g., Zinc-Bromide)	With proper system design & controls	Rated power run time is < 1.5 h per stack	Multiple stacks required
Molten Liquid Battery (e.g., Sodium-Sulfur)			Multiple batteries required for > 8 h
Conventional Batteries (e.g., Li-Ion, Lead-Acid)		Rated power run time is < 1.5 h per battery	Multiple battery strings required
Flywheels, SMES, or UltraCapacitors		Multiple devices required	
Above- or below-ground CAES	Slow response times		
Pumped Hydro	Slow response times		

¹ A conventional FBS is *not* ideally suited for EES applications that require *only* short run times; however, it can be designed to respond very rapidly with proper system design and control.

² The Zinc-Bromide battery is often mistakenly referred to as a *flow battery*. In fact, it utilizes a solid material on the zinc electrode and is, therefore, subject to many of the same limitations as a conventional battery.

Table 1 State of the Art Capability Assessment of Various Known EES Technologies

The VRFB system is a single-metal system which contains a negative half-cell $V_{2\mu}=V_{3\mu}$ redox pair and a positive half-cell $V_{4\beta}=V_{5\mu}$ redox pair. Cross-contamination between semi cells is prevented, as shown in the Fig 2, by using these four separate vanadium oxidation states. Proton migration via diaphragm is the optimal load carrier between the two semi cells, balancing changes in the vanadium oxidation conditions against electrons flowing via the external RFB device circuit.

Chemistry	Redox Reactions	Open-Circuit Voltage (OCV)
All-Vanadium (full flow system)	Negative electrode	1.3
	$V^{3+} + e^- \xrightleftharpoons[\text{Discharge}]{\text{Charge}} V^{2+}$	
	Positive electrode	
	$VO^{2+} + H_2O \xrightleftharpoons[\text{Discharge}]{\text{Charge}} VO_2^+ + 2H^+ + e^-$	
Fe/Cr system	Negative electrode	1.2
	$Cr^{3+} + e^- \xrightleftharpoons[\text{Discharge}]{\text{Charge}} Cr^{2+}$	
	Positive electrode	
	$Fe^{2+} - e^- \xrightleftharpoons[\text{Discharge}]{\text{Charge}} Fe^{3+}$	
Hybrid flow system Zn/Br ₂ system	Negative electrode	1.8
	$Zn^{2+} + 2e^- \xrightleftharpoons[\text{Discharge}]{\text{Charge}} Zn$	
	Positive electrode	
	$2Br^- - 2e^- \xrightleftharpoons[\text{Discharge}]{\text{Charge}} Br_2$	

Figure 2: Basic configurations of flow batteries

As a supporting electrolyte for VRBs, sulphuric acid (H₂SO₄) has been commonly used. The stability and solubility of vanadium species is regulated by optimized H₂SO₄ and vanadium-ion concentrations. There are two key factors influencing the overall concentration of vanadium species: (1) at low temperatures, the solubility of all kinds and possible problems for precipitation and (2) electrolyte freezing; and at high temperatures. The solution is limited by the solubility of vanadium salts [21].

As vanadium oxides, like V₂O₅, have low solubility, the reaction is also called the "thermal precipitation" because of the precipitation resulting in the conversion of the sulphate to the oxide [22]. The kinetics of the proton and water is exchanged in the vanadium ions play a significant role in sulphate anions. The VO₂ becomes the preferred complex by increasing the total sulphate amount (> 5M SO₂[—]). Including traditional VRB electrolytes, which use 1.5–3.0 M of H₂SO₄ and 1.5–2.0 M of vanadium sulphates in conventional electrolytes (the effect is a total sulphates content of 3–5 M) a safe working temperature range of —20 to 40, respectively is in use [23]. The expense of all vanadium electrolytes is a big problem with VRB. Although vanadium is an abundant component of chemically combined forms and relatively low levels in nature, it is inherently more costly than some other redox organisms. Furthermore, vanadium-pentoxide, V₂O₅, must be transformed into valid vanadium sulphate as a VRB electrolyte at the lowest cost of the product vanadium [24]. Many methods for covering V₂O₅ in VRB electrolytes have been planned and the cost of electrolyte preparation has to be further reduced. Flow batteries based on bromine hydrogen (H₂-Br₂) are being designed to increase energy density as well [25]. Initial findings were first published by Yeo and Chin on hydrogen-bromine RFBs in the 1980s. Present focus has been on creating affordable catalysts for the substitution of Pt as a catalyst, improving membranes and stacking designs to stop bromine and bromide cross over. The need to effectively store large quantities of H₂ and binary phases of bromine slurries is a major challenge for large scales implementation of this technology.

Hybrid Flow Systems

At least one of the electrolytes in hybrid flow batteries is often in a fluid state (i.e., dissolved salt in a liquid solvent), and in the other electrolyte solution the electrode species in an electrolyte is deposited with the electrical solution during charge or discharge. The metal is usually used as the charging negative (i.e. oxidation level is zero) on a surface of the negative electrode during the charging [26]. Usually, the metal flow battery is hybrid-battery. Zn/Br₂ and Zn/Cl₂ systems are best known among the hybrid flow technology, with Zn/Br₂ systems most mature, including some limited manufacturing systems and the Zn/Br₂ flow battery's standard configuration. The relatively low material cost, high energy densities (particularly for flow battery systems), and favorable CVs attract Zn-based RFBs [27].

Zinc metal is deposited in the Zn/Br₂ system on the negatives and bronze ions are oxidised in the positive electrodes to elementary bromine. The reversed reaction occurs during the discharge process, resulting in aqueous solutions dissolved in ZnBr₂ and HBr. Elemental bromine blends excess bromide in the solution during the charging process to create complex anons (e.g. br⁻³), resulting in high viscosity two-phase slurry [28]. The toxicity, vapour pressure and aggressiveness of bromide species, which reacts and/or corrodes many materials, are a major concern of the method. Complexing agents may be used to alleviate those problems, but there have been no reports of effects on reaction kinetics and long-term efficacy [29]. This method was considered for transport applications by the mid-1970s until 1992 when an accident at an EV racing event stopped developing this application because of Zn/Br chemistry's attractive energy density. Over the last 20 years, Zn/Br₂-based EES systems have been out. Market acceptance, however, was rather late.

Zn/Cl₂ technology uses a two-phase solid liquid manifold, similar to Zn/Br₂ flow batteries. With the concurrent release of Cl₂ gas at the positive electrode, Zn metal is deposited on the negative electrode surfaces [30]. Chlorinated gas is transported and deposited as chlorine hydrate into a secondary chamber. Zn deposited oxidizes to Zn₂β in the discharge phase and chlorine hydrate is transferred through heat exchangers to reshaping the chlo-driving anions. Although a large number of studies were carried out with regard to Zn/Cl₂ flow batteries, progress was largely limited due to chlorine gas leakage potential [31]. The interest in the hybrid flow battery is also increased, because of the iron metal charging negative reactive.

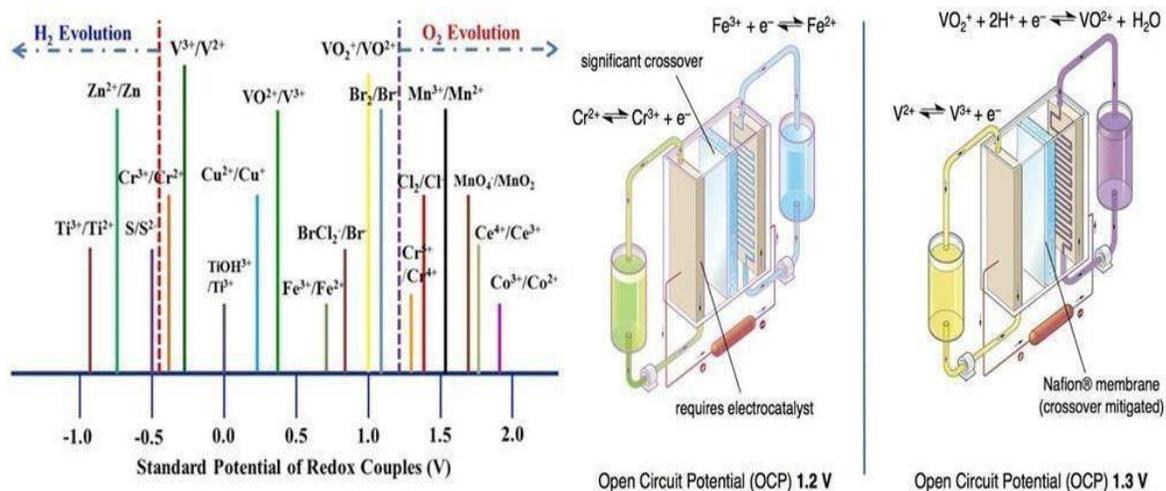


Figure 3: Standard electrochemical potential window for various redox couples and Full-flow systems based on vanadium and FeCr redox couples in aqueous solutions.

RFB System Design Aspects

There are three major subsystems in one full RFB system: 1) cell stacking; 2) electrolyte storage; and 3) plant balance; (BOP). The BOP contains at least these four main components: 1) two positive and negative electrolyte reactant storage tanks; 2) two recirculation loops that supply the reactants between the tanks and the cell stack;

3) one power conditioning system (PCS); and 4) one system controller [30]. During the discharge process, electricity shall be extracted from the cell stack and consumed when charging. The PCS converts the direct current (dc) power from the cell stack to alternative current (ac) power corresponding to the grid voltage and vice versa, respectively, during both operations [32]. The BOP also usually provides for heat discharge produced by cell stack and PCS reactions and various safety equipment. A Battery Management System (BMS) contains the system control to ensure stable operation and optimize the lifespan of the stack and the system. Unwanted side reactions are possible in RFB cells especially if the battery is overloaded or overloaded before redox reactants are exhausted locally as is the case with any battery [33]. Hydrogen and oxygen production, for example, can result from overloading in watery RFB systems. In order to prevent unintended oxidation of cell constituents such as carbohral electrodes and bipolar plates, the cell potential during charging must also be reduced.

The RFB system is operated in three modes: loading, discharge and maintenance of electrolyte. During the loading (and unloading) process, ample quantities of energy are pumped from the electrolyte from the storage tanks to the cell stack to sustain the electrochemistry [34]. The SOC of the electrolyte usually ranges between approximately 80%-85% and 15%-20%. However, reducing energy efficiency and the potential for undesirable side reactions can essentially go well beyond these values, restricting the realistic SOC spectrum. Each pump is pumped using central pumps, normally done with magnetically attached pump heads, so as to avoid leakage or corrosion problems with the solutions of corrosive electrolytes [27]. Electrolyte maintenance is regularly needed to reverse the effects of active cross-sectional species across the cell membrane, usually referred to as "rebalancing." Net solvent transport (e.g., water) across the membrane can also cause changes to electrolyte concentrations, which also affects the total electrolyte volume of each tank. Without this maintenance, cycling would reduce both energy and productivity. The re-equilibrium of the RFB is straight forward; because it consists of simply ensure that the sum for each electrolyte tank of this particular species is about equal [35]. It could be a little more

troublesome in systems where the sum of both different species is not controllable independently even though both reactants are present in both tanks, unless a form of separating procedure, which is not common either, is used. The BOP system contains key commodity elements. It should be noted. BOP contains pumps, plastic plumbing, plastic and power supplies, for example Power supplies. Some items must be

adapted for RFB applications, such as PCS, but they are manufactured massively today and are readily accessible in similar applications from existing supply chains with proven lifetime [36]. In the chemical industry, recirculation pumps for circulating concentrated acids, for instance. In comparison, the cell stack is a custom subsystem composed of custom components, and thus is perhaps from a cost and reliability point of view the most important component.

System Issues and Scalability

Flow batteries are similar in that the reactors in both systems flow past the electrodes. RFBs are typically run in the same way as in the early stage low fuel cells and have a rating of 50–100 mA/cm² as in the case of fuel cells. But electrochemical reactors with flowing electrolytes have a much higher current density and power than traditional batteries because convection by the porous electrode results in a high mass transport rate that cannot match static electrolytes. For example, lead acid batteries are equivalent to VRBs [19] (i.e. lead sulfuric acid sulphate) at a comparable current density. Therefore, considerably higher reaction rates should be expected in battery flow cells, which essentially use the forced flow through the cells [33].

Several groups have recently demonstrated the ability to substantially increase the current and power density of flow batteries. If the stack is run at higher densities, both stack size and overall device costs can fall dramatically as cell stack materials and labour costs are significantly reduced (especially at low production volumes [37], since the cell stack is a custom subsystem built from custom components, unlike most of the other RFB system components that are commodities). These substantial cell performance changes have been made using the same basic material sets as conventional RFB cells with an improved cell design. For example, improved design of the flow field will allow diluted carbon electrodes with excellent mass transport and decreased ohmic losses, as stated in the previous section. In comparison to historical trends, recent cell performance improvements were fast. Cell voltage is separate from current in an ideal cell [38].

However, even in open circuit voltage conditions this is not practically understood because of some irreversibility during cell operation. These include parasites and electrode activation losses, electrode and electrode ohmic losses, mass transportation losses, membrane reactor crossing and shunt currents. Similar to petroleum cells, the cell stack design has a major impact on the entire system's performance. An RFB system is very modular because of the wide variety of main specifications (e.g. total kilowatt and kilowatt-hours) that can be specific for each grid scale EES application. The stacks have a rated power and can be connected as needed in series/parallel. The electrolyte tanks have a rated energy capacity and can be connected as needed in series / parallel. The optimum configuration of a specific EES program needs to be calculated by parasite losses in various device configurations, but such losses have been identified and can easily be predicted. A study was carried out for example, of shunt current losses, pumping losses and other BOP problems for large systems. RFB systems of 50 kW/200 kWh to 4 MW/6 MWh were successfully built and proven with 200 000 cycles proved in the Tomomae wind turbine of Japan for a 4 MW/6 MWh system [39].

Electrode Materials

A significant factor affecting the efficiency of RFB is the proper selection of electrode materials. Electrode materials with properties such as good mechanical strength, high conductivity of electricity, chemistry, corrosion resistance, and side reactions inertness such as the formation of gases, higher redox electrochemical operation and costs need to be considered [40]. High surface area and porosity are another essential property for RFB electrodes. Different types of carbon such as graphite are the most common electrode materials. Carbon felt electrodes have historically been used because they are large scale and stable in watery electrolytes. Polymer-impregnated carbon materials are usually used in the case of the systems Zn/Br₂. Felt electrodes are modified by various techniques such as thermal and chemical processing, as well as electrochemical processing, such as metal doping on the felt electrode surface [26].

All cells, especially large stacks, with a highly compressible material like carbon felt, are difficult to obtain uniform compression. The use of carbon sheets, which are much more rigid than felt. While carbon papers are

usually not as dense as carbon felt materials and thus have less surface area per piece, several groups have claimed that stacking carbon paper layers may produce superior cell efficiency, which is higher than those recorded for carbohydrates. In the long term, carbon paper suppliers are expected to supply thicker carbon papers so that two to three layers of paper are not needed to stack to achieve the optimum electrode thickness [32]. In order to further improve its performance, it is always a field of interest to use additives or metal catalysts in RFB. Electrodes such as those used in Cr-redox. A major requirement is that the performance enhancement of this catalyst be adequate to warrant the increased expense and complexity and should not facilitate side reactions. Several recent advances in this field in relation to VRB systems have been recorded in the production of doped graphite that has reduced the peak to peak separation for the redox pair V₂μ/V₃β by 29 percent. Titanium/iridium (IV) oxides are believed to generate the same catalytic effect with the redox pair V₄ / V₅^{••} (Ti/IRO₂:Ta₂O₅). There is a better risk of using metal-based electrode materials using nonaqueous flow batteries. As a matter of general, [33-36] noble metals are used to prevent unintended production or decomposition of gas in the charging discharging phase, due to their higher electrocatalytic activity and stability. Metal electrodes however suffer from inconveniences such as cost, metal ions dissolution into an electrolyte solution and corrosion.

Membrane/Separator

The most expensive part in the RFB stack (on a \$/m² basis) currently are the Ion Exchange membranes. They play an important part also in the performance of a stack in the RFB, as not only the cathode and anode compartments are separated and the redox species reduce crossover, but the carrier-ion transports also must allow the electrical circuit to be completed [41]. Thus both coulombic and voltage efficiency of an RFB cell have a significant effect on this membrane. Excellent chemical stability, low strength, high permeability and selectiveness for ions, low permeability for electrolytes (including solvents) and strong mechanical and structural strength are ideal characteristics for RFB membranes [42]. In the 1890s the principle of the membrane for ion exchange was first developed. Ion exchange membranes have usually been categorized as anionic and cation exchange membranes, with anion exchange membranes with positive loads (e.g., NH₄⁺, SRβ₂, NRα, NRH β₂) and cation-based exchange membrane containing negatively-loaded groups (e.g. COO⁻, C₆H₄O⁻, SO⁻ 3 PO₃H, PO₂⁻). In the beginning, DuPont designed this membrane for chlorine-alkali applications specifically [43]. The names of these membranes were: "Na" is sodium ion, "f" is fluorinated and ion, as it is the membrane that exchanges ion. Because in both chlorinated and fuel cells there is only one form of cation, selectivity of ion was not necessary. The membrane has also been optimized for optimum ion conductivity, meaning relatively wide pores for hydrophilic pores in which ion transport happens [44]. Not surprisingly, vanadium crossover between

cells is a common problem that causes coulombic efficiency loss and periodic re-equilibrium in VRB systems for electrolyte solution. This unavoidable active species crossover may be even more difficult in RFBs which use different redox species. Unfortunately, there was little interest in designing membranes designed for RFB applications because of the limited commercial prospects for substitutes for Nafion, such as membranes [45]. Their stability in the presence of highly aggressive and oxidative electrical solutions is a big problem with ion-exchange membranes. Oxidizing agents like sulfuric acid and VO_2 are not resisted in most polymeric membranes. However, in these conditions, completely fluorinated IEMs proved to be fairly good. In the recent production of perfluorinated membranes considerable activity occurred in order to boost their stability in application of fuel cells. DuPont Nafion XL membrane, for example, has improved reinforcement, which enhance the handling and physical properties of the membrane [46]. The perfluorosulfonic acid/PTFE chemically stabilised. Additional fluorination therapy and enhancement aid the lower release of fluoride ions and allows longer fuel cell operations [109]. Fuel cells are in some ways more aggressive than RFB cells. The two key failures are mechanical loss resulting from long relatively humid cycles of fuel cells, which leads to swelling, contracting and chemical degradation of the membrane by producing radicals free of charge. Neither of these mechanisms of degradation should be essential in RFB cells. In addition, foreign cation contamination after 40 000 hours of service is the most common failure mechanism of these membranes in chlor-alkali cells. In RFB cells, this should also not be a major concern, as an RFB is a closed system, as opposed to chloroalkalic cells, which constantly have fresh reactants containing trace contamination, inevitably. Consideration of all these factors into account, in addition to relatively low operating temperatures, is positive about the life of fluorinated

ion exchange mucosa in RFB cells [47]. Some attempts have been made to use potentially lower cost membranes including polyvinylidene fluoride (PVDF), but additional ion permeability functionalities were required. In FeCr systems with appropriate ion selectivity and chemical and mechanical stability, non-fluorinated polymer membranes have had some success. Separators with micropores are commonly used in the processes of waste water treatment in lead-acid and lithium ion battery. Differently than the ion-exchange membrane, microporous separators operate because they use pores in size and thickness to distinguish the ions between the two half cells. Separators with high punch resistance, strong ion selectiveness and high ionic transports have become popular for their high electrical resistance [48]. There are only a few examples of RFBs, such as daramic separators and nanofiltration membranes that have been demonstrated. Separators have low ion conductivity and selectivity relative to ion-exchange membranes and are around 10 percent less efficient overall. Until RFB implementations can be implemented, the long-term stability, crossover, and chemical stability must be further studied.

Table 2 provides a variety of different energy storage technologies and a comparison of these technologies for different applications. The inherent drawbacks or disadvantages in each technology make them feasible or economical for a small range of applications alone. Electric chemicals are considered superior to other energy storage systems that are largely mechanical in their design, and thus have relatively long response times compared to batteries and electrochemical condensers when comparing performance with cost. Electrochemical energy storage systems provide direct conversion between energy from chemical sources and electricity and thus are especially suitable for storing power from all sources [50]. Electrochemical storage solutions also provide additional benefits over other energy storage systems, like anywhere, unlike geologically or geologically defined hydro or compressed air systems. They are modular, so it can be used from a few kWh up to several MWh for applications. With millisecond reaction times, both energy efficiency and energy control applications can be used at the same time. Have low footprints, so they can be found in residential areas.

Table 2. Comparison of technicalities of different energy storage devices as against the redox flow battery

Energy storage technology	Discharge duration (h)	Response time	Efficiency (w/o power electronics)	Capital Cost (\$/kWh)	Life (y)	Cycle life at 80% depth of discharge	Maturity	Limitations
Pumped hydro	> 8	Very good	70–85%	80–200	30	20,000–50,000	Commercial	Special geological and geographic requirements
Superconducting magnet	0.25	Good	90–95%	10,000	30	1000–10,000	Commercial	Needs a long loop to achieve commercially useful levels of storage
Compressed Air energy storage	0.1–15	Very good	60–79	50–110	30	9,000–30,000	Demonstration stage with limited commercial	Special geological and geographic requirements
Flywheel	0.1–1	Slow	> 90%	300–5,000	20	> 20,000	Commercial	Low energy density
Super-capacitors	0.02–1	Good	> 95%	82,000	low	10,000–100,000	Almost commercial	Low energy density, Unable to use full energy spectrum and high self-discharge
Thermal Energy storage	1–45	Slow	60%	\$500/kW	20	4000–10,000	Commercial	large investments required to build the initial infrastructure
Lead-acid batteries	0.1–4	Fast	70–76%	350–1500	5–10	200–1500	Commercial in smaller systems. Several MW scale demonstrations	Low to medium Energy density. Poor deep discharge performance
Sodium sulphur batteries	1–10	Fast	85–90%	300–950	5–10	210–4500	Commercial More than 50 multi-kW to MW scale demonstrations	Poor thermal cycling

Lithium ion batteries	0.1–1	Fast	> 90%	850–5,000	5–10	5,000–7,000	Commercial in small Scale appliances. Several MW-scale demonstrations	High cost
Flow batteries	1–20	High	75–85%	180–250	> 10	5,000–14,000 ^b	Almost commercial. More than 20 multi-kW to MW Scale demonstrations. Several companies setting up commercial manufacture	Low to medium energy density. Require more parts (such as pumps) compared with other types of batteries

Cost, Performance, and Reliability Metrics

As discussed earlier, there are currently many cost estimates for redox flow batteries available. The cost is normally provided at \$/kWh, without the actual output of the storage device for a specific application being taken into consideration. Section VI-A demonstrates some of the efficiency indicators [51]. Most energy storage systems have a quick response time and should not be limited to this metric. Here, as regards the size of energy storage, only the effective discharge must be used as the square source of energy efficiency for all journeys. This enables the cell stack to be calculated to provide the necessary power and the electric tanks to provide the necessary energy. Optimization of operating conditions such as flow rate, drainage depth, SOC ranges and current densities may allow the cost of system for a particular EES application to be calculated [52].

In terms of \$/kWh per discharge period, EES device costs are usually recorded. Cost varies depending on the system's energy ratio. In case of an energy/power ratio specifying costs in \$/kW or \$/kWh and, preferably, \$/kW and \$/kWh for the required components, along with a \$/kWh sum, it is desirable to disclose the energy/power ratio individually. In RFB systems we should remember that the components of \$/kW and \$/kWh differ with

their energy or power ratio and that for longer download times we often get the best overall cost (\$/kWh), as more power only takes extra reactants which cost less than the whole system at a \$/kWh rate. In this respect, the cost of RFB systems scales very differently than conventional battery systems, which require the addition of both reactants and inactive materials to add energy capacity [54]. RFB systems will be most cost competitive for energy-intensive EES applications, especially those that require long lifetimes with thousands of deep discharge cycles.

Flow Battery Limitations, Challenges and Future Research Opportunities

Despite significant technological developments in the field, the full market potential of flow battery technology for grid and mobile systems can only be realized once a number of challenges have been overcome. In particular, the production of electrode resistant materials and improving electrolyte stability are addressed to a broader temperature range. In order to better optimize the effect of cell geometry on its cell efficiency and on the development of oxygen and hydrogen, several mathematical models have been designed for simulating the effect of all redox flow batteries and steps to prevent gas output. Advanced modeling and simulation will help to build advanced control systems that will enable large

VRB systems to operate remotely, automatically rebound electrolytes and capacities, while improving the electrolyte flow rate to reduce the demands of the pumping energy and improve overall energy efficiency.

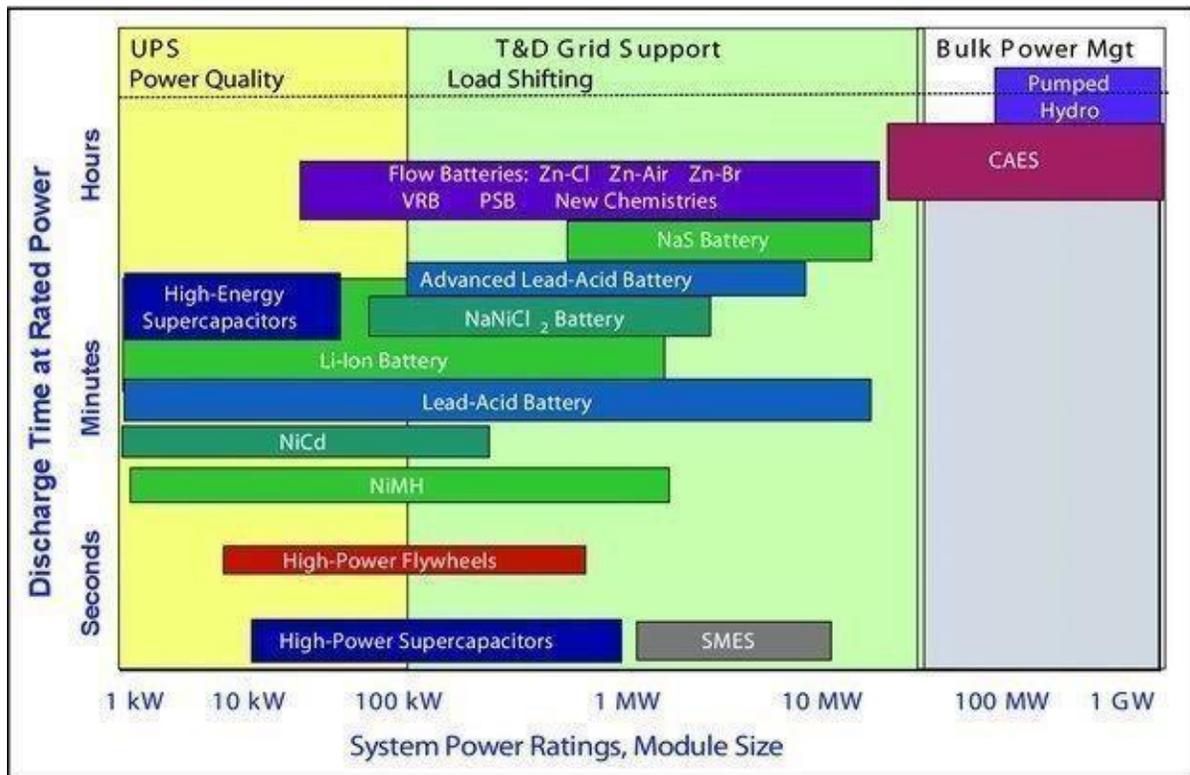


Figure 4: Performance and charged- discharged time comparisons of RFBS

Reduction of cost of capital and cycle life is also important if all energy storage technologies are to be taken commercially in broad terms [53]. The ionic exchange membrane has been reported to be the most costly part of the all vanadium redox battery and thus significant research is under way to develop cost efficient alternatives. A updated perfluorinated membrane substrate material costing Nafion less than one third and providing a pricing structure appropriate for most applications [33]. Tested in battery stacks of 5-10 kW and 80% energy efficiency, this new membrane has been refined. A number of research groups in China and the USA are developing new, low price membrane ion exchange materials which promise to further reduce the costs in a broader range of grid applications to meet the requirements of cost structure.

Conclusion

Flow batteries have a clear benefit in that energy and power can be scaled independently, which makes them flexible in a wide variety of applications, ranging from firming to frequency control and linked to local distributed generation applications in large grid systems. Cost and reliability are the main problems to be overcome to realize these benefits on a business basis. Substantial advances in RFB technology have been made in recent years and, due to the comparatively limited amounts of research dedicated to this technology, the speed of improvements will continue to outweigh those in the traditional batteries. Therefore, flow batteries are unique to a variety of applications, including storage for renewable energy sources, for instance wind, solar (photovoltaic), wave, remote surface replacement, power supplies (rapps), including load level diesel backup generators and peak shaving storage for transmitting power and smart grid systems. There are several ways in which active material prices can be lowered. Based on

ligand modified redox pairs and organic species, new aqueous electrolytes are being produced that give the potential of whole new groups of flow reactants. The new electrolyte needs to be readily available, stable, low viscosity and non-corrosive to achieve a lower cost, so that low cost cell pilot materials cannot be used and relatively high efficiency cell stacks can be carried out using the new flow battery types, Nonaqueous electrolytes provide a chance for increasing energy density and lower costs per kilowatt-hr. New research in this field is exciting and of course, there are more continuous activities in this field today than in the last 30 years.

Recent significant improvements in RFB cell efficiency are also expected to lead to significant cost reduction for inactive materials, because state of the art cell stacks are much smaller and require less material. Although Nafion is the membrane material used for the most battery cells, alternatives are beginning to be produced at low cost and/or higher efficiency. Fresh, low cost materials are often used to decrease costs for stacks of structural elements with designs that allow easy quick assembly. Advanced computer modeling is capable of optimizing the fluid flow channels for large cross sectional stacks and can help predict pressures and other parasite losses. Recent developments have also been made in software control and device diagnostics for optimizing battery management systems, leading to more improvements in the overall power efficiency and reliability of the system. While low system costs are important for decreasing capital outlay costs, cycle life is crucial for reducing the overall energy costs of an EES device over its lifetime. Usually, the cycle life of more than 5 000 to 10 000 cycles would cost \$/kWh of energy, in line with the current energy sources generated using fossil fuels. Another way to improve cyclical life is to combine renewable energy sources and energy storage with the provision of electricity at a fossil fuel consumption rate.

References:

- [1] Zame, K. K., Brehm, C. A., Nitica, A. T., Richard, C. L., & Schweitzer III, G. D. (2018). Smart grid and energy storage: Policy recommendations. *Renewable and Sustainable Energy Reviews*, 82, 1646-1654.
- [2] Lucas, A., & Chondrogiannis, S. (2016). Smart grid energy storage controller for frequency regulation and peak shaving, using a vanadium redox flow battery. *International Journal of Electrical Power & Energy Systems*, 80, 26-36.
- [3] Zhang, C., Wei, Y. L., Cao, P. F., & Lin, M. C. (2018). Energy storage system: Current studies on batteries and power condition system. *Renewable and Sustainable Energy Reviews*, 82, 3091-3106.
- [4] Hu, X., Zou, C., Zhang, C., & Li, Y. (2017). Technological developments in batteries: a survey of principal roles, types, and management needs. *IEEE Power and Energy Magazine*, 15(5), 20-31.
- [5] Palizban, O., & Kauhaniemi, K. (2016). Energy storage systems in modern grids—Matrix of technologies and applications. *Journal of Energy Storage*, 6, 248-259.
- [6] Colmenar-Santos, A., Muñoz-Gómez, A. M., Rosales-Asensio, E., & López-Rey, Á. (2019). Electric vehicle charging strategy to support renewable energy sources in Europe 2050 low-carbon scenario. *Energy*, 183, 61-74.
- [7] Bamgbopa, M. O., Almheiri, S., & Sun, H. (2017). Prospects of recently developed membraneless cell designs for redox flow batteries. *Renewable and Sustainable Energy Reviews*, 70, 506-518.
- [8] Vasilyev, A. (2019). Modelling polymer electrolyte membrane fuel cells for dynamic reliability assessment (Doctoral dissertation, Loughborough University).

- [9] Zolotovskiy, K. (2017). Guided growth: design and computation of biologically active materials (Doctoral dissertation, Massachusetts Institute of Technology).
- [10] Lu, C., Hoang, T. K., Doan, T. N. L., Zhao, H., Pan, R., Yang, L & Chen, P. (2016). Rechargeable hybrid Aqueous batteries using silica nanoparticle doped aqueous electrolytes. *Applied Energy*, 170, 58-64.
- [11] Zanzola, E. (2020). Aqueous Redox Flow Batteries Enhanced by Solid Boosters (No. THESIS). EPFL.
- [12] Meng, F. L., Liu, K. H., Zhang, Y., Shi, M. M., Zhang, X. B., Yan, J. M., & Jiang, Q. (2018). Recent advances toward the rational design of efficient bifunctional air electrodes for rechargeable Zn–air batteries. *Small*, 14(32), 1703843.
- [13] Yao, J., Li, Y., Massé, R. C., Uchaker, E., & Cao, G. (2018). Revitalized interest in vanadium pentoxide as cathode material for lithium-ion batteries and beyond. *Energy Storage Materials*, 11, 205-259.
- [14] Cao, D., Sun, X., Li, Q., Natan, A., Xiang, P., & Zhu, H. (2020). Lithium Dendrite in All-Solid-State Batteries: Growth Mechanisms, Suppression Strategies, and Characterizations. *Matter*.
- [15] Li, C., Liu, L., Kang, J., Xiao, Y., Feng, Y., Cao, F. F., & Zhang, H. (2020). Pristine MOF and COF materials for advanced batteries. *Energy Storage Materials*.
- [16] Arora, S. (2018). Selection of thermal management system for modular battery packs of electric vehicles: A review of existing and emerging technologies. *Journal of Power Sources*, 400, 621-640.
- [17] Abdalla, A. H. (2017). Iron-based Rechargeable Batteries for Large-scale Battery Energy Storage (Doctoral dissertation, University of Sheffield).
- [18] Pang, H., Cao, X., Zhu, L., & Zheng, M. (2020). Nanomaterials for Batteries. In *Synthesis of Functional Nanomaterials for Electrochemical Energy Storage* (pp. 107-193). Springer, Singapore.
- [19] Meyerson, M. L. (2020). Studies of electrode materials for lithium and sodium metal batteries (Doctoral dissertation).
- [20] Hartle, L. A. (2018). Atmospheric Pressure Chemical Vapor Deposition of Fluorine-Doped Tin Oxide and Tin-Germanium Oxide: Photovoltaic and Energy Storage Applications (Doctoral dissertation).
- [21] Xiao, S., Yu, L., Wu, L., Liu, L., Qiu, X., & Xi, J. (2016). Broad temperature adaptability of vanadium redox flow battery—Part 1: Electrolyte research. *Electrochimica Acta*, 187, 525-534.
- [22] Ye, R., Henkensmeier, D., Yoon, S. J., Huang, Z., Kim, D. K., Chang, Z. & Chen, R. (2018). Redox flow batteries for energy storage: a technology review. *Journal of Electrochemical Energy Conversion and Storage*, 15(1).
- [23] Jirabovornwisut, T., & Arpornwichanop, A. (2019). A review on the electrolyte imbalance in vanadium redox flow batteries. *International Journal of Hydrogen Energy*, 44(45), 24485-24509.
- [24] Nibel, O. (2017). Component development for all-vanadium redox flow batteries: Membrane design and cell characterization (Doctoral dissertation, ETH Zurich).
- [25] Taylor, S. M. (2017). Investigation of the Electrochemical Reactions Involved in All-Vanadium Redox Flow Cells (Doctoral dissertation, ETH Zurich).
- [26] Suresh, S., Ulaganathan, M., Venkatesan, N., Periasamy, P., & Ragupathy, P. (2018). High performance zinc-bromine redox flow batteries: Role of various carbon felts and cell configurations. *Journal of Energy Storage*, 20, 134-139.
- [27] Yang, H. S., Park, J. H., Ra, H. W., Jin, C. S., & Yang, J. H. (2016). Critical rate of electrolyte circulation for preventing zinc dendrite formation in a zinc–bromine redox flow battery. *Journal of Power Sources*, 325, 446-452.
- [28] Xu, Z., Wang, J., Yan, S. C., Fan, Q., & Lund, P. D. (2020). Modeling of Zinc Bromine redox flow battery with application to channel design. *Journal of Power Sources*, 450, 227436.
- [29] Suresh, S., Ulaganathan, M., Aswathy, R., & Ragupathy, P. (2018). Enhancement of bromine reversibility using chemically modified electrodes and their applications in zinc bromine hybrid redox flow batteries. *ChemElectroChem*, 5(22), 3411-3418.
- [30] Xu, Z., Fan, Q., Li, Y., Wang, J., & Lund, P. D. (2020). Review of zinc dendrite formation in zinc bromine redox flow battery. *Renewable and Sustainable Energy Reviews*, 127, 109838.
- [31] Wu, M. C., Zhao, T. S., Jiang, H. R., Zeng, Y. K., & Ren, Y. X. (2017). High-performance zinc bromine flow battery via improved design of electrolyte and electrode. *Journal of Power Sources*, 355, 62-68.
- [32] Arenas, L. F., De León, C. P., & Walsh, F. C. (2017). Engineering aspects of the design, construction and performance of modular redox flow batteries for energy storage. *Journal of Energy Storage*, 11, 119-153.

- [33] Shigematsu, T. (2019). The development and demonstration status of practical flow battery systems. *Current Opinion in Electrochemistry*, 18, 55-60.
- [34] Muhammad, R. D., Herlambang, S., Dwi, L., & Muhammad, Y. Y. (2017). Modal Analysis and Stability Enhancement of 150 kV Sulsebarbar Electrical System using PSS and RFB based on Cuckoo Search Algorithm. *International Journal on Electrical Engineering and Informatics*, 9(4), 800-812.
- [35] Li, W., & Jin, S. (2020). Design Principles and Developments of Integrated Solar Flow Batteries. *Accounts of Chemical Research*, 13104-13108.
- [36] Guarnieri, M., Trovò, A., D'Anzi, A., & Alotto, P. (2018). Developing vanadium redox flow technology on a 9-kW 26-kWh industrial scale test facility: Design review and early experiments. *Applied Energy*, 230, 1425-1434.
- [37] Milshtein, J. D., Darling, R. M., Drake, J., Perry, M. L., & Brushett, F. R. (2017). The critical role of supporting electrolyte selection on flow battery cost. *Journal of the Electrochemical Society*, 164(14), A3883.
- [38] Zeng, Y., Yang, Z., Lu, F., & Xie, Y. (2019). A novel tin-bromine redox flow battery for large-scale energy storage. *Applied Energy*, 255, 113756.
- [39] Guarnieri, M., Trovò, A., D'Anzi, A., & Alotto, P. (2018). Developing vanadium redox flow technology on a 9-kW 26-kWh industrial scale test facility: Design review and early experiments. *Applied Energy*, 230, 1425-1434.
- [40] Leung, P., Palma, J., Garcia-Quismondo, E., Sanz, L., Mohamed, M. R., & Anderson, M. (2016). Evaluation of electrode materials for all-copper hybrid flow batteries. *Journal of Power Sources*, 310, 1-11.
- [41] Hery, T., & Sundaresan, V. B. (2016). Ionic redox transistor from pore-spanning PPy (DBS) membranes. *Energy & Environmental Science*, 9(8), 2555-2562.
- [42] Michos, I., Cao, Z., Xu, Z., Jing, W., & Dong, J. (2019). Investigations on a Mesoporous Glass Membrane as Ion Separator for a Redox Flow Battery. *Batteries*, 5(1), 6.
- [43] Sankarasubramanian, S., Zhang, Y., & Ramani, V. (2019). Methanesulfonic acid-based electrode-decoupled vanadium–cerium redox flow battery exhibits significantly improved capacity and cycle life. *Sustainable Energy & Fuels*, 3(9), 2417-2425.
- [44] Gandomi, Y. A., Aaron, D. S., & Mench, M. M. (2016). Coupled membrane transport parameters for ionic species in all-vanadium redox flow batteries. *Electrochimica Acta*, 218, 174-190.
- [45] Gubler, L. (2019). Membranes and separators for redox flow batteries. *Current Opinion in Electrochemistry*, 18, 31-36.
- [46] Ding, Y., Zhao, Y., Li, Y., Goodenough, J. B., & Yu, G. (2017). A high-performance all-metallocene-based, non-aqueous redox flow battery. *Energy & Environmental Science*, 10(2), 491-497.
- [47] Rajarathnam, G. P., & Vassallo, A. M. (2016). Description of the Zn/Br RFB System. In *The Zinc/Bromine Flow Battery* (pp. 11-28). Springer, Singapore.
- [48] Kosswattaarachchi, A. M., & Cook, T. R. (2018). Repurposing the industrial dye methylene blue as an active component for redox flow batteries. *ChemElectroChem*, 5(22), 3437-3442.
- [49] Nonjola, P. T., Mutangwa, N., & Luo, H. (2016). Membrane Separators for Electrochemical Energy Storage Technologies. In *Nanomaterials in Advanced Batteries and Supercapacitors* (pp. 417-462). Springer, Cham.
- [50] Kushner, D. I., Crothers, A. R., Kusoglu, A., & Weber, A. Z. (2020). Transport phenomena in flow battery ion-conducting membranes. *Current Opinion in Electrochemistry*, 21, 132-139.
- [51] Hossain, M. S., Hossain, M. I., Jahangir, T., & Hasan, M. A. *Icrrd High Index Research Journal*.
- [52] Lüth, T., König, S., Suriyah, M., & Leibfried, T. (2018). Passive components limit the cost reduction of conventionally designed vanadium redox flow batteries. *Energy Procedia*, 155, 379-389.
- [53] Minke, C., Hickmann, T., dos Santos, A. R., Kunz, U., & Turek, T. (2016). Cost and performance prospects for composite bipolar plates in fuel cells and redox flow batteries. *Journal of Power Sources*, 305, 182-190. [54] Li, B., & Liu, J. (2017). Progress and directions in low-cost redox-flow batteries for large-scale energy storage. *National Science Review*, 4(1), 91-105.