A Review on Redox Flow Batteries

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Abstract

This paper presents a literature review about the concept of Redox Flow Batteries (RFBs), their principal operations, and composition. The working of the RFB and the concepts related to the kinetics of redox reactions is presented. The main focus is on presenting the most common type of RFB, i.e., vanadium redox flow batteries (VRFBs), which have several benefits compared with other existing technologies and methods for energy stored purposes. A study is described in which, compared to other types of energy storage systems, redox flow batteries are contextualised in the current energy situation. The main aspects reviewed in this work correspond to the composition and operation of VRFBs consisting of a membrane and electrode. The research proposed in the past literature and its disadvantages and advantages were also presented.

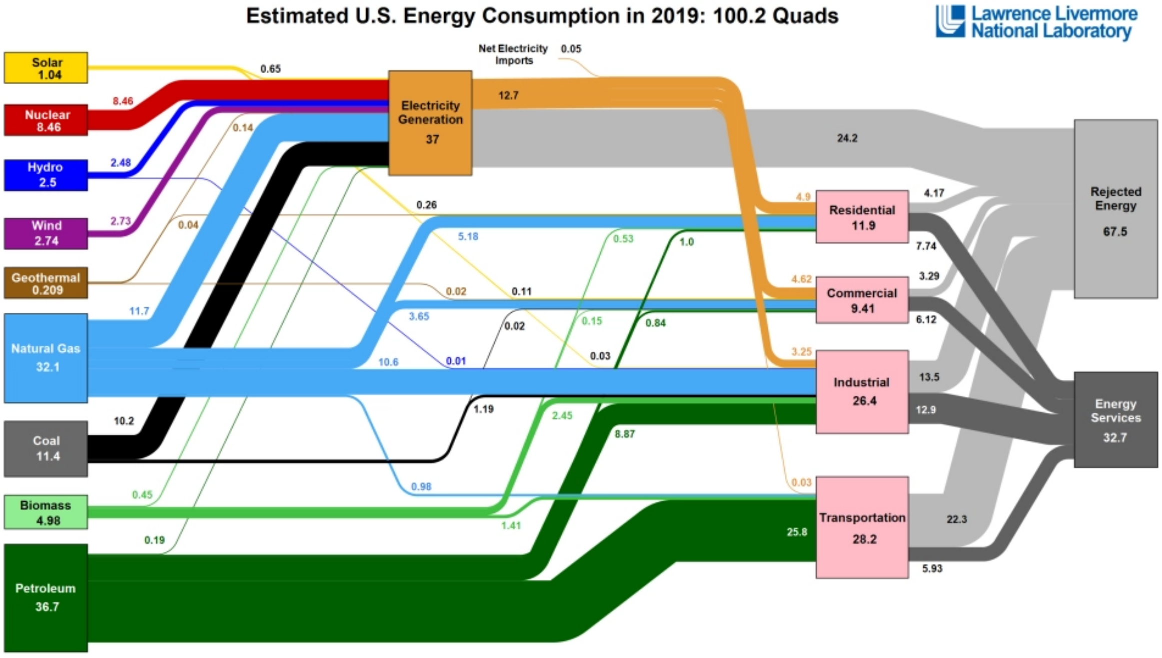
1. Introduction

Most of the electricity in today's world is generated by the consumption of non-renewable fuel resources that are expected to last up to 40 to 70 years, so there is a significant challenge to produce electricity using some easy and cost-effective renewable energy sources. The world has developed various method after this challenge was noticed, such as solar energy, wind energy, nuclear energy and tidal energy. However, all these methods are not perfect in one way or another. For instance, solar and wind energy could be affected by unpredictable nature, nuclear energy has safety and environmental issues. Therefore, other renewable energy sources like Redox Flow Batteries (RFBs) are trending and an emerging topic of research and development to meet the needs of the increasing demand for energy.

Electricity demand is rising by 2.4% each year along with the increasing emissions of greenhouse gases, thereby leaving the current centralized system with the needs for upgrading and re-evaluation. Decentralized energy is electrical generation and storage performed by a variety of small, grid-connected or distribution system connected devices. These resources are a class of technologies that could aid in this regard and are evolving as an alternative or complementary to centralized generation and as a potentially significant feature of future power systems. RFBs have the ability to store a large amount of electrical energy effectively and economically, hence it could be one typical type of decentralised energy suppliers.

A challenge faced by every nation is the high cost of constructing an electricity grid and the high cost of the energy transfer process at a distance. New emerging concepts such as ‘smart grids’ and ‘microgrids’ can effectively provide new economic benefits [1]. It considers a fair economic settlement scheme for participants in a microgrid, which is a special case of the smart grid concept. It can also be improved by the participation of RFBs as a decentralised energy generator which could aid excess energy back into the grid. RBFs have the benefits through interconnection and coordinated control, and environmental benefits using low carbon/low pollutant generation and co-production of heat and power, which could serve as a cleaner energy resource.

Figure 1 shows the 2019 US energy flowchart released by Lawrence Livermore National Laboratory (LLNL). As shown on the right side of the graph, rejected energy is a major problem and accounted for 67.4% of total output; a significant amount of energy was wasted in transmission due to electrical resistance in wires. Among all components of rejected energy, the 'Electricity Generation' resulted the highest of 24.2 quadrillion BTU (or quads). In the same way that using trams could decrease the percentage of rejected energy in 'Transportation', the participation of RBFs in 'Electricity Generation' could reduce the distance of energy transfer hence reduce the amount of rejected energy.

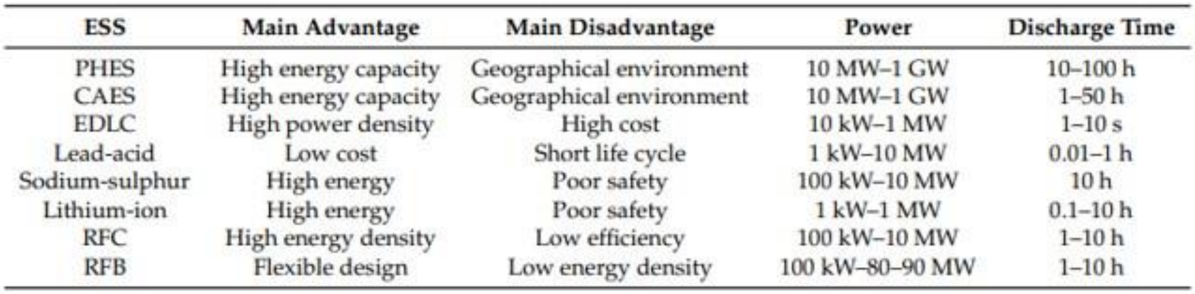

Estimated U.S. Energy Consumption in 2019: 100.2 Quads

Source: LLNL March, 2020. Data is based on DOE/EIA MER (2019). If this information or a reproduction of it is used, credit must be given to the Lawrence Livermore National Laboratory and the Department of Energy, under whose auspices the work was performed. Distributed electricity represents only retail electricity sales and does not include self-generation. EIA reports consumption of renewable resources (i.e., hydro, wind, geothermal and solar) for electricity in BTU-equivalent values by assuming a typical fossil fuel plant heat rate. The efficiency of electricity production is calculated as the total retail electricity delivered divided by the primary energy input into electricity generation. End use efficiency is estimated as 65% for the residential sector, 65% for the commercial sector, 21% for the transportation sector and 49% for the industrial sector, which was updated in 2017 to reflect DOE's analysis of manufacturing. Totals may not equal sum of components due to independent rounding. LLNL-MI-410527

Figure 1. Lawrence Livermore National Laboratory (LLNL) 2019 US energy flow chart.[2]

The need for an Energy Storage System (ESS) is mandatory in order to meet the demand for energy at times of low energy output [6][7]. ESS can store and supply energy, typically surplus energy from renewable sources, when environmental conditions do not make it possible to produce all the necessary energy. Hence, ESS is seen as an essential constituent of clean energy source, combined with power generation systems, such as photovoltaic or wind systems.

Apart from the load-levelling, another significant advantage is the function of ESS as a support element for the electricity grid's generation and distribution lines [8][9]. During periods of Renewable Energy Sources (RES) low production, ESS can increase the available power considerably and in terms of capacity and time, it can be used for large-scale energy storage system solutions to guarantee the energy supply. The main ESS's principal characteristics are summarized in **Table 1** based on advantages, disadvantages, power, and discharge time excerpted from Chen's work [11].



ESS	Main Advantage	Main Disadvantage	Power	Discharge Time
PHES	High energy capacity	Geographical environment	10 MW–1 GW	10–100 h
CAES	High energy capacity	Geographical environment	10 MW–1 GW	1–50 h
EDLC	High power density	High cost	10 kW–1 MW	1–10 s
Lead-acid	Low cost	Short life cycle	1 kW–10 MW	0.01–1 h
Sodium-sulphur	High energy	Poor safety	100 kW–10 MW	10 h
Lithium-ion	High energy	Poor safety	1 kW–1 MW	0.1–10 h
RFC	High energy density	Low efficiency	100 kW–10 MW	1–10 h
RFB	Flexible design	Low energy density	100 kW–80–90 MW	1–10 h

Table 1. Main ESS advantages, disadvantages, power, and discharge time. [11]

The most common ESS are pumped hydro energy storage (PHES) and compressed air energy storage (CAES) systems within the mechanical large-scale ESS category due to their main advantage of high energy capacity [12]. PHES is system which stores energy in the form of potential energy of water that is pumped from a lower reservoir to a higher-level reservoir [75] with PHES having 70-80% efficiencies and in some installation cases up to 90%. Whereas CAES is a technique for supplying electric power to meet peak load requirements of electric utility systems [76]. Also, the PHES systems are the most extensive form of grid energy storage capacity available, becoming the type of active plant with the highest capacity with more than 184 GW worldwide in 2017, comprising 95% of all operational tracked storage facilities [13]. As for the drawbacks, stable geological structures are needed by both PHES and CAES, which significantly restrict the use of this type of device [11], while CAES also has the limitation that its energy efficiency is less than 70%, even reaching values below 45% as published [14][15]. The superconducting magnetic energy storage (SMES) device is a novel technology that stores electricity from the grid within the magnetic field of a coil comprised of superconducting wire with near-zero loss of energy [77].

It is focused on the use of electromagnetic energy, and the electrical double-layer capacitor (EDLC), which directly uses electrical energy, are the most common for large-scale electric ESS [16], being about 90% efficiency of SMES the main advantage [17]. The key downside is the high cost of superconducting wire, which makes this technology more suitable for short-term applications, with the refrigeration energy that this system requires [18]. EDLC's key benefits are that it can produce large quantities of power and its long-life cycle (supporting more than one million charge and discharge cycles). On the other hand, they have a low energy density and, due to the self-discharge phenomenon, they can only retain energy for short periods [19]. The last category of ESS, which refers to the storage of energy from chemical reactions, comprises numerous batteries and new technologies. Lead-acid, sodium-sulfur, and lithium-ion are common batteries that have been used for many years. The strengths of lead-acid batteries are their low cost and excellent efficiencies ranging from 75% to 80% [20], but they have a limited life (between 200 and 1800 cycles of charge and discharge) and are toxic [21]. But it is important to remark, on the global scale, persistent lead (Pb) pollution has been considered a significant threat to human health due to its exposure through numerous pathways and may cause potential human health hazards, various organ disorders. As demonstrated in Dumat's work [3], the scientific research regarding potential adverse health effects of Pb and its low energy efficiency makes its use much more limited. With comparable efficiencies, sodium-sulfur has a higher energy capacity than lead-acid batteries, but with a longer lifespan of about 2500 cycles [22][23], but this type of technology's main problem is its operating temperature (about 300 ◦C) and a poor safety due to possible leaks of the liquids inside it.

Finally, compared to the previously named ones, lithium-ion batteries are the better option [24], having a greater energy density and a long life, more than 2500 cycles [25]. Although lithium iron phosphate batteries solutions produced by A123 System had almost twice the specific energy than nickel-metal hydride batteries used in current hybrid vehicles, these batteries have a short durability of 2 to 3 years from the date of manufacture no matter whether intensely used or not. They degrade even faster if exposed to heat compared to the normal temperature exposure because these lithium-ion batteries are susceptible to high temperatures and are ruined if fully discharged [4].

Presently, more research is being done within the electrochemical ESS category, especially in fuel cells and redox flow batteries. Compared to the conventional cells (batteries) where energy is stored in the electrode material, the flow cells store energy in the electrolyte solution. Via an electrochemical reaction between the fuel and an oxidizing agent, fuel cells transform chemical energy from fuel into electric energy [26]. RBFs is a type of fuel cell, which is a rechargeable reduction-oxidation cell, where electrochemical components are dissolved in the electrolyte solution having the key benefits of being clean ESS. Typical power efficiency values vary between 40% and 60% [28]. In terms of cost, reliability, and protection, RFBs are promising for stationary large-scale applications in various energy storage systems [5]. Energy is converted into electrochemical reactions and deposited in external tanks by maintaining the active electrolyte species. The energy density of the RFBs is calculated by the electrolyte volume, the active species concentration, the voltage of the cells, and the number of stacks. The ability to produce power is linked to the kinetic role of active redox species and the size of the electrodes. These make the RFBs flexible systems for energy storage.

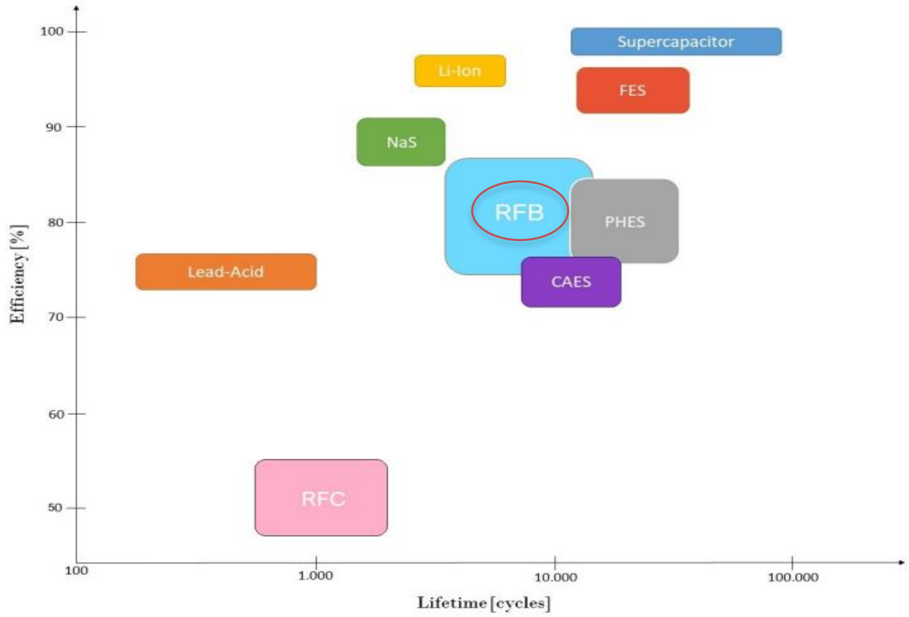


Figure 2. Efficiency and lifetime comparison of main energy storage systems. [32]

The link between energy capacity and power is one of the key characteristics of RFBs and Redox Flow Cells (RFCs). Energy capacity is a function of the electrolyte volume, which is typically contained in tanks, and depends on the volume and concentration of the electrolyte that can provide energy for minutes to hours [29]. The power is directly related to the surface property of the electrodes and the number of system-composing cells [30]. The crucial advantages of RBFs include safety, flexible design, long life, large-scale storage applications, and practically non-existent self-discharge. RFBs have charge/discharge efficiency values of between 75% and 85% [31], which surpass RFCs with relatively low efficiencies. For that reason, comparing with RFCs, RFBs are a great recommendation for large-scale ESS. They are better than classic batteries such as lead-acid, sodium-sulfur, and lithium-ion in terms of protection. RFBs are also the right choice if they are compared in terms of efficiency and lifespan, as can be seen in **Figure 2**.

Comparison of RFBs with other ESSs, taking **Table 1** into account, as in PHES and CAES systems, RFBs allow large quantities of energy to be distributed over long periods, without the need for a precise geographical location. RFBs benefit from their greater lifespan, protection, and low cost compared to lithium-ion batteries with high energy density, and therefore RFBs have become one of the most promising choices in electrochemical ESS [33]. In terms of working principles, RFBs differs from lithium-ion technology in the link between power and energy capacity, whereas lithium-ion batteries do not contain any active elements from an automatic control point of view and thus do not need any control [34].

This review introduces essential concepts and an overview of RFBs, their working principles and essential components, with a well-known example of RFB - vanadium redox flow battery (VRFB), considering the great opportunities that RFBs offer as large-scale storage systems and the numerous studies that are being carried out on them so far. The organization of the review paper is as follows: Section 2 shows the overview, working principle of an RFB and kinetics of redox reaction; Section 3 presents an example of a RFB, *i.e.* VRFB, its composition, membrane and electrode explanation, Section 4 is the summary containing the limitations and existing solutions for the problems, conclusion and future development followed by references.

2. Redox Flow Battery

2.1 Overview

Among various energy-storage schemes being developed worldwide, Redox Flow Batteries (RFBs) are one of the most promising. RFBs are cheap, reliable energy storage batteries that can store large amounts of power safely and efficiently. They can be used on a large-scale, *e.g.*, in a power station, or more locally as a smaller storage bank for a house or dwelling (similar to the Tesla Powerwall concept). RFBs can be characterized by active or solvent species (aqueous and non-aqueous, respectively). In the active electrolyte species, energy is converted into electrochemical reactions and deposited in external tanks.

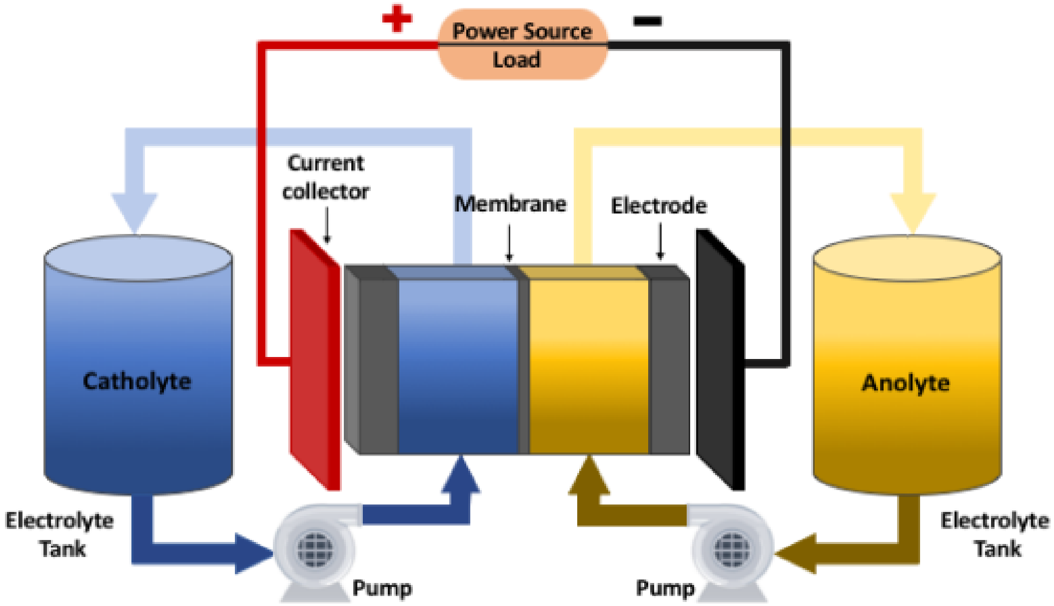


Figure 3. A schematic diagram of a redox flow battery with electron transport in the circuit, ion transport in the electrolyte and across the membrane, active species crossover, and mass transport in the electrolyte.[35]

Figure 3 shows a schematic diagram of a redox flow battery. An anolyte solution flows through a porous electrode in the discharge mode and reacts to produce electrons that flow through the external circuit. The species carrying the charge are then transported to a separator distinguishing the anolyte and catholyte solutions (typically an ion-exchange membrane (IEM)) [36] and the general reaction can be formulated as below, for the anode (A: negative electrode) and cathode (B: positive electrode), respectively.

$$\mathrm{A}^{n+} + xe^{-} \rightarrow \mathrm{A}^{(n-x)+}\text{where } (n > x) \text{ while charging}$$

$$\mathrm{A}^{(n-x)+} \rightarrow \mathrm{A}^{n+} + xe^{-} \text{ while discharging}$$

$$\mathrm{B}^{m+} - ye^{-} \rightarrow \mathrm{B}^{(m+y)+} \text{ while charging}$$

$$\mathrm{B}^{(m+y)+} \rightarrow \mathrm{B}^{m+} - ye^{-} \text{ while discharging}$$

Other than the charge-transfer reaction kinetics, the dominant energy efficiency losses in these systems are related to the charge and mass transport in the electrolyte and the separator; however, the crossover of species through the separator, which is based on current and membrane permeability, is a critical factor in several of those systems.

2.2 Working principle of redox flow batteries

RFB works by charging and discharging an electrolyte solution, usually containing reversible electrochemical ion pairs (such as V^{2+}/V^{3+}), with both the oxidized and reduced ions being soluble in the liquid electrolyte. Electron exchange at an electrode/electrolyte interface oxidizes or reduces the electrolyte, such that the electrical energy is stored chemically by changing the oxidation state of the metal ion. A practical RFB consists of two different electrolytes, circulating in their own space, separated by an Ion-Exchange Membrane (IEM). An anode or a cathode is placed into each solution, respectively, forming an electrochemical ‘converter cell.’ The IEM is usually a Nafion-like membrane that prevents the anode and cathode solutions from mixing and stops contamination and short circuit between electrodes while allowing ion exchange to occur between the solutions.

Throughout the charge or discharge process, the required amount of two liquid electrolytes depends only on the relative concentrations of the oxidized and reduced solution of each flow and, thus, the energy storage potential of the RFB. Since these can be stored in 2 large reservoirs (100s of litres) located some distance away, the energy storage can be huge (10 W/kg & 70 kWh/kg) with the electrolyte circulated to and from the working converter cell via pumps [70]. The power is a function of the surface area of the two electrodes, which can be porous or microstructure electrodes. The cell voltage is chemically determined by the Nernst equation (i.e., the identity and concentration of the electrolytes) and usually ranges from 1.0 - 2.2 V.

2.2 Kinetics of redox reactions

To understand the concepts of redox reactions fundamentally, the study of the kinetics of redox reactions holds a pivotal place in electrochemistry. The most important ideas were developed from the consideration of redox reactions in the theory of electrode reactions. A one-electron transfer of an electron to or from an electrode to an ion in solution is the simplest type of a redox reaction, written generally as:

$$\mathrm{O} + ne^- \rightleftharpoons \mathrm{R}$$

where O is the oxidized state and R the reduced state of the ion. There are no modifications in the ion in the simplest form of the redox reaction other than the condition of valence and solvent relaxation around the ion. The prototypical example of such a reaction is the ferrous/ferric reaction in sulfuric acid solutions and the involvement of the theory is more complicated when the ions are complexed with neutral or other anions that do not participate in the electron transfer directly [36]. Many of the basic concepts of electron transfer kinetics can be found in classic electrochemical texts such as Vetter's work [37] which provides a unique explanation of the history of the growth, including the familiar names of Butler and Volmer, of the fundamental theory of electrode kinetics, and [38] which gives the Butler–Volmer model of the kinetics of reactions producing the essential current (i) over potential (η) relationship as:

$$i = i_0\left[\left(\frac{\mathrm{c_O}(0,\mathrm{t})}{c_O^*}\right)\exp\left(\propto\frac{F}{RT}\eta\right) - \left(\frac{\mathrm{c_R}(0,\mathrm{t})}{c_R^*}\right)\exp\left(-(1-\propto)\frac{F}{RT}\eta\right)\right]$$

$$\eta = \Phi_k - \Phi_p - E_{eq}$$

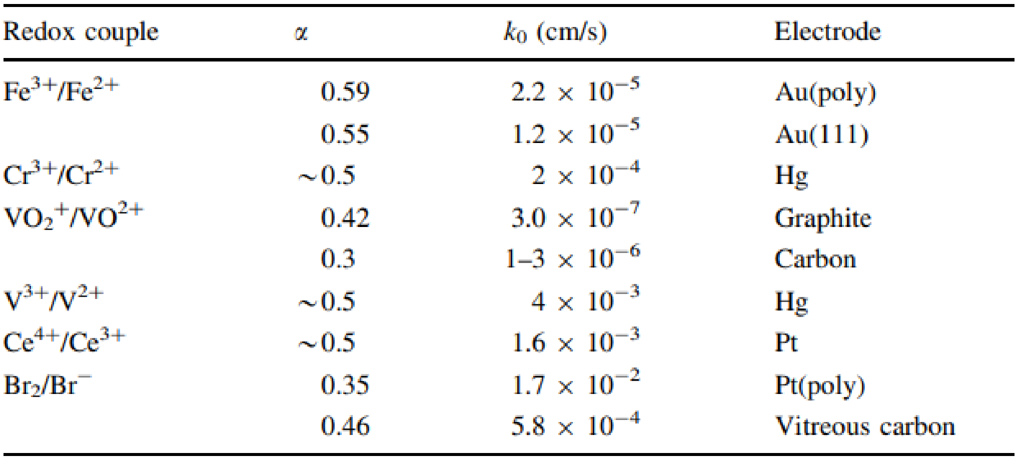
Where η is the overpotential, defined as the difference between the electrode potential under current flow and the rest (zero current) potential and where $\Phi_k$is the potential in phase k, and E_{eq} is the Nernst potential, which is related to the concentrations of the oxidized (c_{O}^*) and reduced (c_{R}^*) species by

$$E_{eq} = E^0 + \frac{RT}{F}ln\left(\frac{c_O^*}{c_R^*}\right)$$

Here, i_o is the exchange current density, α is the transfer coefficient (or the symmetry factor in transition-state theory) [36]. For both basic (experimental) kinetic studies and for modelling practical devices, this form of the Butler-Volmer equation is essential since the contribution of mass transport of the ions from the bulk solution to the electrode surface needs to be considered in both cases. Exchange current density and the transfer coefficient are the critical kinetic parameters calculated experimentally. The exchange current is the magnitude of the partial anodic and cathodic currents that are equal at equilibrium and are related to the bulk concentrations by the standard rate constant k^0.

$$i = Fk^0 c_0^{*(1-\alpha)} c_R^{*\alpha}$$

Since the exchange current density varies with the concentration of the redox species, the more fundamental measure of kinetics for redox reactions is k^o . The approximate order of magnitude of the kinetic rate can be estimated for a practical RFB. For instance, RFB must have a high electrical efficiency of at least 80 % round-trip or 90 % in each direction and assume a standard cell voltage of 1.5 V; then, during the charge/discharge cycle, the kinetic overpotential must be less than 150 mV. The exchange current density must be greater than 0.3 mA/cm^2 during the charge/discharge period, assuming a minimum practical current density of at least 50 mA/cm^2, a roughness factor of 10, i.e., 10 cm^2 surface per unit electrode geometric area, and a transfer coefficient of 0.5. Assuming 1 M solutions at 50% state of charge and assuming 90% utilization of the redox ions in the cycle, the minimum value of the standard rate constant k^0 is ~ 10^{-5} cm/s [36].



Redox couple	α	k_0 (cm/s)	Electrode
Fe^{3+}/Fe^{2+}	0.59	2.2×10^{-5}	Au(poly)
	0.55	1.2×10^{-5}	Au(111)
Cr^{3+}/Cr^{2+}	~0.5	2×10^{-4}	Hg
VO_2^+/VO^{2+}	0.42	3.0×10^{-7}	Graphite
	0.3	$1–3 \times 10^{-6}$	Carbon
V^{3+}/V^{2+}	~0.5	4×10^{-3}	Hg
Ce^{4+}/Ce^{3+}	~0.5	1.6×10^{-3}	Pt
Br_2/Br^-	0.35	1.7×10^{-2}	Pt(poly)
	0.46	5.8×10^{-4}	Vitreous carbon

Table 2. Kinetic parameters for redox reactions used in flow batteries where supporting electrolyte in most cases is 1 M H_2SO_4, or $HClO_4$ and concentration of redox species is 10^{-3} to 10^{-2} M. [36] [37][39][40][41][42][43][44][45]

If the rate constant is substantially lower than this value, to achieve a functional system that can improve cost and/or utility, some compromises must be made. For instance, higher surface area/porosity electrodes will compromise a simple flow-by/through design. And reduced current density will reduce power density and result in larger electrodes and more material per unit volume in the RFB. Thus, **Table 2** can be related to the value estimated above with those already in the literature. **Table 2** shows that among the practical RFBs currently in use, only the VO^{2+}/VO_2^+ redox couple has a clear kinetic limitation. This is not unusual as redox is not a simple one-electron transfer reaction but an oxygen transfer reaction in modern terms. The kinetic data in Gattrell's work [42] were obtained using a graphite rotating disk electrode (RDE): the polarization curves shown for V^{2+}/V^{3+} indicated a rate constant >> 10^{-5} cm/s.

3. Vanadium Redox Flow Battery (VRFB)

3.1 Overview

Over the past few decades, numerous metal-based redox couples have been examined as chemical electrolytes for RBFs [46]. Among them, vanadium RFBs (VFRBs) were mostly investigated in which supporting electrolyte is sulfuric acid and with maximal energy density about 30 WhL^{-1}. The energy density is constrained by the solubility and stability of four vanadium ions (VO_2^+, VO^{2+}, V^{2+} and V^{3+}), and this can be marginally improved using mixed sulfate-chloride electrolytes [47]. Another threshold to be mentioned is that vanadium ion crossovers through the membranes would reduce the efficiency of the cells and involve electrolyte remixing [30]. Therefore, low vanadium permeability, high Coulombic efficiency (CE) and high energy efficiency (EE) membranes are required.

In most recent studies, carbon-based electrodes are used to catalyse the redox reactions of VO^{2+}/VO_2^+ and V^{2+}/V^{3+} and are prominent because of their relatively low cost and high performance. The surface area and the number of active functional groups on the surface can be increased by analytical processing and modification of the carbon electrode with, for example, TiO_2 or MnO_2 nanosheets [11][48]. Catalyst particles on the surface of the carbon electrode will further encourage kinetics and increase voltage efficiency (VE) [49].

Alternative energy-dense electrolytes could be identified to increase the energy storage potential of RFBs with a high concentration of active species and high cell voltage [50]. Efforts have recently been made to use low-cost, environmentally friendly organic and polymer electrolytes [51] in energy storage systems and suspension electrolytes with solid active species [52]. In order to optimize VRFBs and build new electrolyte and cell systems for practical use, several challenges need to be overcome, including a fundamental understanding of electrolyte electrochemistry, the development of improved electrode materials, and creativity in the crucial aspects of cell and stack design [30].

3.2 Composition and Operation of Vanadium Redox Flow Batteries

RFBs are secondary batteries and work on the principle of energy conversion, from the electrochemical reactions of two redox couples. Redox reaction phenomenon is an exchange of electrons between two different species by oxidation and reduction process and can be interpreted as [35]:

Oxidation: an enhanced state of oxidation of a species due to the loss of one or more electrons.

Reduction: decreased state of oxidation of a species caused by one or more electrons being gained.

The operation of RFB in detail was explained in Section 2. A redox flow battery consists of two electrodes and functions at the surface where the oxidation-reduction reactions occur. In the case of non-carbon electrode materials such as metals, it was found that both half-cells were unsuitable for metal materials [53]. For both electrodes of a VRFB, carbon has been identified as the best material and numerous studies have been conducted to evaluate its usage and benefits [54][55].

Because of the presence of two collector plates located at the end of the cell, current due to the electrons from the redox reaction flows, and the direction of current flow depends on whether the battery is charging or discharging. Typically, depending on the configuration of the VRFB, standard values of current densities differ from 10 mA/cm^2 to 800 mA/cm^2 [56]. Using a Nafion membrane, typical current density values differ only in a window between 80 mA/cm^2 and 140 mA/cm^2 with efficiencies varying from 80 % to 90 %, since lower efficiency is observed to increase the current density above 150 mA/cm^2 due to higher ohmic resistance of the Nafion membrane [57]. The restriction of the maximum current density for VRFB was evaluated in various tests, obtaining 750 mA/cm^2 for three layers of carbon fibre paper [58].

One of the key advantages of RFBs is that the electrolytes are found within the cell and stored in two separate tanks. The electrolytes are composed of a particular concentration of the active species and are dissolved in a strong acid solution, usually hydrochloric acid (HCl) or sulfuric acid (H_2SO_4). The positive electrolyte (catholyte) and negative electrolyte (anolyte) are stored in separate anti-corrosion tanks. Fluids are pumped through the battery stack from the tanks holding the electrolytes into two closed circuits (consisting of multiple flow cells stacked together), and the redox reaction occurs at the electrode sides. Because of the closed flow circuit, the post-reaction species are recirculated to the corresponding opposite tank [35].

The electrolytes in a VRFB contain vanadium salts dissolved in concentrated sulfuric acid solutions. Four oxidation states of vanadium ion are involved in their redox reactions (+II, +III, +IV, +V) [59]. V^{2+} and V^{3+} vanadium species make up the negative electrolyte (anolyte). V^{4+} and V^{5+} make up the positive electrolyte (catholyte). Usually, the highest concentration of vanadium ion that can be used for a large temperature range activity is 2 M [11][60] and this concentration is equivalent to an energy density of around 25 W h/kg. Even at temperatures below 5°C, this value ensures the solubility of vanadium ions. Simultaneously, vanadium ion stability is guaranteed at potential temperatures above 40 °C [61]. The V^{4+} oxidises to V^{5+} during the charging phase, releasing an electron. This electron is passed through the external circuit from the anode to the cathode and reduces V^{3+} to V^{2+} on the other electrode. The oxidation of V^{2+} to V^{3+} takes place in the negative electrolyte (anode) during the discharge process, and the released electron goes to the cathode, reducing V^{5+} to V^{4+}. The V^{4+} and V^{5+} vanadium species exist as oxides, VO^{2+} and VO_2^+, respectively. In the cell, the chemical reactions that take place are the following:

$$\mathrm{V}^{2+} \rightleftharpoons V^{3+} + e^-$$

$$\mathrm{VO_2}^+ + 2\mathrm{H}^+ + e^- \rightleftharpoons \mathrm{VO}^{2+} + \mathrm{H_2O}$$

where → represents the charge process, and ← represents the discharge process [35]. The standard cell potential E^{Θ} can then be written as:

$$E^{\Theta} = E^{\Theta}_{\text{cathode}} - E^{\Theta}_{\text{anode}}$$

Chemistry reaction tables [35][62] describe each half-reaction phase's standard potential under standard strain, concentration, and temperature conditions. The standard potential for the case of the VRFB is:

$$V^{2+} \rightleftharpoons V^{3+} + e^{-} \qquad E^{\Theta}_{\text{anode}} = -0.255\text{ V}$$

$$VO_2^{+} + 2H^{+} + e^{-} \rightleftharpoons VO^{2+} + H_2O \qquad E^{\Theta}_{\text{cathode}} = 1.004\text{ V}$$

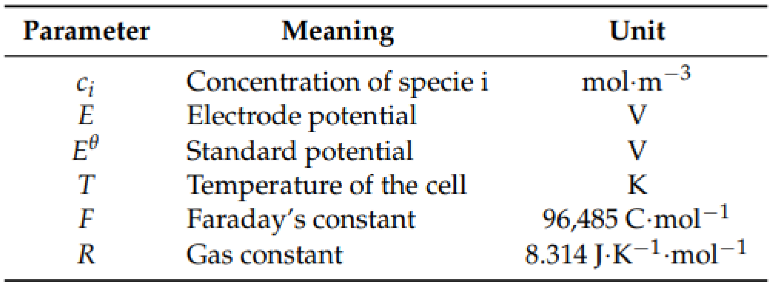
Taking the above equations into account, the overall reaction obtained from both reactions can be written together, with its cell standard potential [35]:

$$V^{2+} + VO_2^{+} + 2H^{+} \rightleftharpoons VO^{2+} + V^{3+} + H_2O \qquad E^{\Theta} = 1.259\text{ V}$$

The potential of the electrode E depends on the concentration of vanadium species c_i in the cell. Its value can be obtained using the Nernst equation:

$$E = E^{\theta} + \frac{RT}{F}\ln\left[\left(\frac{c_{VO_2^{+}}C_{H^{+}}^{2}}{c_{VO^{2+}}}\right)_{catholyte} \cdot \left(\frac{c_{V^{2+}}}{c_{V^{3+}}}\right)_{anolyte}\right]$$

where R and F are the gas constant and Faraday constants, respectively, and c is the concentration of each vanadium species found in the catholyte or anolyte electrolyte shown in **Table 3**.



Parameter	Meaning	Unit
c_i	Concentration of specie i	$\text{mol}\cdot\text{m}^{-3}$
E	Electrode potential	V
E^{θ}	Standard potential	V
T	Temperature of the cell	K
F	Faraday's constant	$96{,}485\ \text{C}\cdot\text{mol}^{-1}$
R	Gas constant	$8.314\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

Table 3. Parameters and constants for Nernst Equation [35].

Using the Nernst Equation, it is possible to calculate the theoretical value of cell voltage, which only depends on the concentration of vanadium. It is necessary to consider that the VRFB's theoretical open-circuit voltage (OCV) has two extreme values that correspond to the complete or null charge state of the cell. These extreme values are far from those measured experimentally in both cases (theoretically tend to infinity). The extreme values of the OCV are, for this reason, experimentally considered. Many studies agree that the maximum value of the cell voltage is between 1.6 and 1.7 V during the charge and decreases to 1.1 V in the discharge case [63][64]. It can be calculated from the experimental value that the single-cell voltage of VRBF is not high. In order to increase power capacity, several cells have to be linked in series, obtaining what is generally called a stack. As the number of all cell voltages are connected in series, the stack's total voltage can be determined.

3.3 Membrane

The membrane prevents the positive and negative electrolyte solutions from mixing inside the VRFB cell [65][66]. It is also referred to as a separator, and two forms are usually used in VRFBs: the membrane for ion exchange and the membrane for nanofiltration [67]. The membrane must promote the redox reaction by allowing charged ions like (H^+, SO_4^{2-}) to pass through, stabilize, and complete the net reaction while also preventing the electrolyte solution's cross-mixing [65]. The membrane is essential for maintaining high efficiency over several cycles in flow battery applications, and membrane performance significantly affects net energy efficiency and the trade-off between chemical stability and conductivity is the biggest challenge that the membrane portion faces [66].

Alteration of the membrane to increase its resistance to the oxidizing conditions of the VRFBs reduces the membrane's ionic conductivity [65][66]. Other factors that are important to the cell's functioning are the thickness and pore size of the membrane. Increasing pore size to increase proton conductivity will improve effectiveness but also increase vanadium crossover. The membrane's thickness is critical because the thinner the membrane, the lower the ion's flow resistance when moving through the membrane [68]. The thickness of the membrane must also be balanced, as the membrane's elastic strength would be decreased by a thinner membrane, rendering it susceptible to tearing during cell compression/operation [66].

3.4 Electrode

The electrode is the part that facilitates the oxidation and reduction reactions. The electrode surface catalyses the reaction, and its porous surface gives the reaction site for the electrolyte solution [69]. Common VRFB implementations have separated positive and negative electrodes (reactions shown in Section 3.2). The electrodes should have a high surface area and/or porosity to have many reaction sites and a triple phase boundary for the flow battery to perform optimally [66][70]. To effectively react and charge the electrolyte flowing through a circuit, the electrode material should be highly catalytic to the redox species. However, due to the high acidity of the electrolyte solution (most electrolytes are sulfuric acid-based), the electrode material must have a good corrosion resistance while maintaining electrical conductivity [70][71].

It is essential to consider both electrode geometry and electrolyte flow when designing a VRFB. These two factors will regulate the overall mass transport and, therefore, the battery's performance. The relationship between mass transport and the input flow rate for the set channel sizes and shape was discussed in Rivera’ work [72]. To have a high current, the surface area and current density of the electrode material should be maximized, all without jeopardizing any of the other VRFB components [72]. Graphitized polyacrylamide (PAN) and rayon (cellulose fibres), in carbon paper and felt forms, are two of the most common electrode materials used [73]. Due to the materials' diverse structure and advantageous chemical properties, carbon-based materials intended for electrodes have been widely researched over previous years [74]. Good design means that the losses can be reduced as much as practicable inside the electrode.

4. Summary

4.1 Limitations of RFB

A considerable problem with RFBs that are in use today is that they normally use a vanadium-ion-based (V^{2+}/V^{3+}) aqueous electrolyte. Unfortunately, vanadium is the most expensive component of these RFBs due to its low abundance in the Earth. The second issue with current RFBs concerns the electrodes, which are typically composed of porous graphite, other materials based on graphene and activated carbon (*i.e.* sp^2 carbon) have also been reported. Such materials are often mechanically weak and degrade with time and need to be regularly replaced. The considerable cost and inconvenience of regularly changing these electrodes is a major obstacle preventing the widespread uptake of RFBs – particularly the smaller household variety.

4.2 Conclusion

In this review, the general introduction of redox flow batteries (RFBs), their working principles, and the chemical reactions and kinetic mechanism of RFBs are covered. The working principles of the most common type of RFB, i.e., vanadium RFBs, their theory and operation and design, along with limiting factors, are explained. RFBs are promising and competitive technologies for possible applications of stationary energy storage. By developing new active redox couples with high concentration, high cell voltage, and rapid reaction kinetics, RFBs with high energy and power densities can be obtained. Device improvements can come from enhanced electrolyte compositions and more useful membrane, electrode, and bipolar plate materials. Although the VRFB is a good choice of decentralised energy storage system, certain limitations and vulnerabilities still exist, like the high cost of the system, the thermal precipitation within the electrolyte, the small energy density that can be achieved in the electrolyte, and the deterioration of sulfuric acid and vanadium that can occur under extreme environment.

4.3 Future Scope and Development

There is no 'most reliable' RFB chemistry at present, but progress continues through government and industry-supported industrial and academic research. Looking to the future, in the study of RFB systems, there are different directions. Within the field of control and supervision, research in terms of flow management and parameter estimation will continue to grow as given in Clemente's work [35]. As in other electrochemical-power-conversion systems, many material degradation modes will likely be associated with transport processes that can be better optimized to promote longevity.

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