Hydropower-Centric Renewable Integration: Advancements in Sustainable VRFB Technology for Energy Storage Solutions

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Abstract. The urgent need to address climate change has prompted a shift from fossil fuels towards green energy sources, such as hydropower for reducing greenhouse gas emissions. All-vanadium redox flow battery (VRFB) is suitable for large-scale energy storage, aimed at stabilizing the renewable energy output. However, VRFB faces challenges in terms of membrane design, electrode performance, and environmental impact. This article provides a comprehensive review of key components in VRFB technology, namely electrodes, membranes, and bipolar plates, discussing their working principles, designs, and recent research findings. The critical role of Nafion® membranes is explored, as they impact both performance and environmental implications. Several strategies are discussed to mitigate the environmental impact, such as alternative membrane materials and protective coatings. The article emphasizes the potential development of VRFB systems as an adaptable and effective energy storage solution for hydropower applications while acknowledging the necessity of sustainable practices for their broader adoption.

Keywords: Green energy, All-Vanadium Ion Redox Flow Battery, Design Nafion® membrane, Modifications of each component, Impact on the environment.

1. Introduction

Climate change is a pressing environmental issue primarily driven by the emission of greenhouse gases. The persistent dependence on non-renewable sources such as coal, natural gas, and petroleum has been propelled by the escalating energy demand. In the United States, the energy landscape reflects this trend with around 78% of energy stemming from fossil fuels, while renewable sources contribute to merely 13% of the overall energy generation [1]. Renewable energy sources, including wind, hydropower, solar, and tidal energies, have gained substantial traction as they offer widespread technologies capable of generating sustainable, reliable, and high-quality electricity. Unfortunately, these renewable sources produce inconsistent, delayed and extremely unpredictable electricity [2]. Hence, direct transportation via the power grid may not be an ideal method. Nevertheless, a favorable solution to address this challenge involves transforming fluctuating energy power into a storable pattern through energy conversion techniques.

There are several vital characteristics that the selected storage technique should consider and fulfil.

Scalability determines the maximum capacity in order to maintain a steady discharge time from hours up to weeks or even months, particularly during periods of heightened energy demand.

Response time is important in actual applications; immediate generation of energy power possesses more options and makes the type of storage more versatile.

The *cost* associated with each component of an energy storage system significantly impacts its feasibility for industrial implementation. A lower cost allows for increased production by multiple companies, fostering healthy competition that can subsequently drive down prices, resulting in more affordable electricity for consumers.

Efficiency is quantified as the disparity between input and output power. However, energy losses incurred during storage, like self-discharge, friction, or chemical side reactions, can result in diminished efficiency. Enhancing efficiency is crucial to ensure that more generated energy is effectively transported to the power grid framework.

Sustaining a *long-life expectancy* while maintaining the capacity of the technology is paramount for effective renewable energy production. This not only minimizes daily maintenance requirements but also reduces operational costs over time. Under regular operational conditions, most energy storage methods have minimal impact to the environment. However, concerns arise when internal hazardous components are released or exposed to the surroundings. In *Section 3*, an illustration is provided using a VRFB as an example, highlighting how the entire system is managed during operation to prevent from potential risk of damage and leakage.

Table 1. Types of energy storage and limitations towards hydropower station application.

Energy storage techniques	Limitations
Flywheel (FES)	● Energy loss due to friction during operation, and frequent maintenance required to replacement of the components. ● Short discharge time unsuitable for renewable energy storage.
Compressed air (CAES)	● Geographical limitations. ● Comparatively low efficiency.
Fuel cell (FC)	● Short lifespan [2]. ● Costly to build up the system and the unit-generated energy.
Lithium-ion battery (LIB)	● Safety issues with organic-based electrolytes. ● Extra monitoring and regulation systems are required to prevent thermal runaway due to the sensitivity of working temperature and voltage window [3]. ● Market-dependent price of lithium.
Lead-acid battery (LAB)	● Safety issues with toxic lead and explosion might occur when the system is overheated. ● Structural degradation if not fully charged (sulfation effect) [4]. ● Short usable life-cycles and replacements bring extra costs.
Thermal (TES)	● Short discharging time due to self-discharge effect via heat exchange. ● Poor long-term cycling stability due to heat corrosion [5].

Presently, the most prevalent energy storage techniques encompass mechanical options (such as Pumped Hydro Energy Storage (PHES), FES, and CAES), electrochemical solutions (including FC, LIB, LAB, and Redox-Flow Batteries (RFB)), and TES. Despite years of investigation and study, selecting the appropriate energy storage method for hydropower stations hinges on an assessment of their advantages and limitations. For instance, PHES currently dominates global large-scale energy storage with a 95% share, but it still has its drawbacks in that PHES necessitates access to substantial water bodies like lakes and entails using considerable land area to establish extensive infrastructure. In the context of hydropower applications, *Table 1* compiles the key limitations of these technologies. Consequently, these applications will not be further discussed within the scope of this article.

RFB is reliable and effective based on the fluid nature of its electrolytes, which provides the system with significant physical flexibility [6]. It was gaining more attention due to lower capital and cycle costs than other storage technologies. Among the various available RFBs, VRFB offers a distinct advantage which they eliminate the cross-contamination issue based on the use of the same material (vanadium (V)) in both electrolytes. In other RFB types (e.g., Fe/Cr, V/Br), cross-contamination arises from concentration gradients across the membrane, leading to self-discharge and decreased storage capacity. Once this happens, these other systems also require electrolyte replacement, incurring additional maintenance costs. In VRFB, the self-discharge problem is resolved through recharging the system simply. *Section 2.31* delves into detailed improvements on the membrane, particularly focusing on the widely used Nafion® membrane. However, the VRFB technology also requires certain improvements to address its drawbacks. For instance, the temperature regulation

system maintains the temperature at 10-40°C. This precaution is vital to prevent the undesirable precipitation of vanadium electrolytes [7].

Given the benefits and balance with its limitations, VRFB represents an exceptionally suitable option for hydropower stations due to their potential to significantly enhance both adaptability and efficiency. VRFB excels in harnessing the variable flow of water, enabling precise control of generator speed to effectively match fluctuating conditions and optimize the energy conversion process [8]. The swift response of VRFB to variations in water flow and grid frequency ensures the stability of the hydropower station, guaranteeing an uninterrupted energy supply. Furthermore, VRFBs are renowned for their remarkable recyclability and extended operational lifespans, relying on recyclable alloys and standard electronics [9]. This environmentally friendly attribute further solidifies VRFBs as a highly desirable energy storage alternative for hydropower stations. In the following article, the working principle of overall *(Section 2.1)* and each vital component *(Section 2.2-2.4)* of the VRFB will be discussed, and the parameters that determine the performance of the cell and their corresponding improvements will be analyzed and summarized based on the recent research paper, and future directions are supposed as well. The manipulations of the system in order to reduce the potential risk of producing V_2O_5 precipitate and replacement of a more sustainable membrane other than Nafion® will also be mentioned in *Section 3*.

2. Literature review

2.1. General working principle

VRFB falls within the category of electrochemical systems. It has the capability to convert electrochemical energy into electricity or vice versa through a series of reactions that leverage varying reduction potentials. The fundamental principle of VRFB shares similarities with other battery types (e.g., LIB, KIB etc.). However, a notable distinction is that in VRFB, the liquid-state electrolytes are contained in two separate tanks positioned away from the reaction centre. The flow of electrolytes is managed by external pumps, allowing for power adjustment during electricity generation or absorption throughout the charging/discharging processes. The primary components of VRFB encompass V ions existing in four distinct oxidation states (V^{4+} as VO^{2+}, V^{5+} as VO_2^+, V^{2+} and V^{3+}). These ions are segregated between the cathodic and anodic electrolytes. In the course of operation, the electrolytes are pumped into two separate half-cells and subsequently returned to their respective tanks for recirculation (as depicted in *Fig. 1*). Upon injection into the half-cells, the two reactions are presented in *Eq. 1* and *Eq. 2*, with the overall reaction illustrated in *Eq. 3*, as shown below:

$$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O \qquad Eq.1$$

$$V^{2+} \rightleftharpoons V^{3+} + e^- \qquad Eq.2$$

$$VO_2^+ + V^{2+} + 2H^+ \rightleftharpoons VO^{2+} + V^{3+} + H_2O \qquad Eq.3$$

During the discharge phase, electrons migrate along the internal electric circuit from the anode to the cathode. Simultaneously, there is also a movement of the proton from the anodic electrolyte to the cathodic electrolyte, essential to uphold the neutrality of the two half-cells. This interplay of electron and proton movement is crucial for completing the circuit during the charge/discharge process.

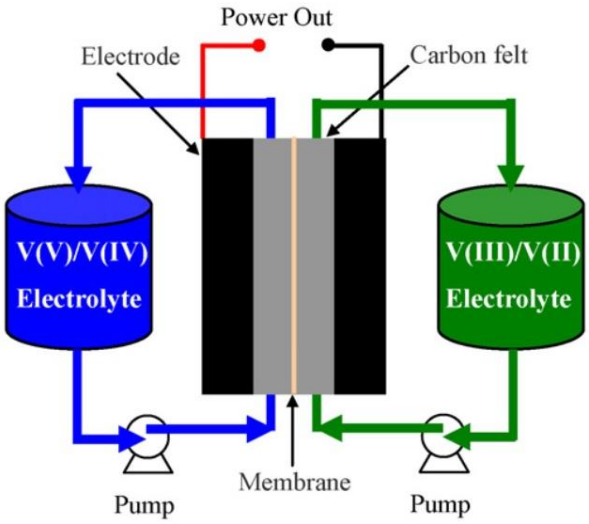

Figure 1. Schematic diagram of VRFB [10].

2.2. Electrode

2.2.1. Working principle

The electrode serves as the site where redox reactions occur in the VRFB cell. The electrode's surface is characterized by its porosity, it catalyzes the reactions and provides the electrolyte solution with reaction sites [11]. In the VRFB, the cathode and anode catalyse redox reactions and conduct electrons. The variance in reduction potentials of two redox reactions generates a potential difference across the two sides of the circuit, thereby initiating the movement of electrons.

2.2.2. Electrode design

As depicted in the comprehensive reaction, all vanadium species can dissolve in the electrolyte, enabling them to effectively participate in the reaction. To attain the highest possible cell potential, it is essential that the disparity between the two redox potentials be substantial. Consequently, the stability of materials in various phases throughout the redox process becomes crucial. For optimal performance of the VRFB, modified electrodes must meet several criteria dictated by the electrolyte conditions. The electrode with a larger surface area facilitates the reaction kinetics.

Nonetheless, the presence of a supporting acidic electrolyte renders the operational environment corrosive [7]. As a result, the electrode material must exhibit robust resistance to corrosion. Additionally, the chosen electrode material should possess robust catalytic properties with respect to the redox species. This catalytic characteristic enhances the efficiency of the reaction and facilitates effective electrolyte charging [7]. In conclusion, electrodes are typically composed predominantly of carbon-based materials [7].

Designing a VRFB involves careful consideration of two key factors: electrode geometry and electrolyte flow. These factors play a pivotal role in determining the battery's efficiency by influencing overall mass transport. Prior to upscaling the system, developers need to focus on two critical aspects. First, it's essential to ensure the controllability of reactions. Second, a clear understanding of the interplay between ion diffusion and the flow rate, considering the size of the transport tunnels and their shapes is imperative. To achieve a high current output while safeguarding other components within the VRFB, the electrode material should be chosen to maximize both surface area and current density. This balance is crucial for optimizing the battery's performance [12].

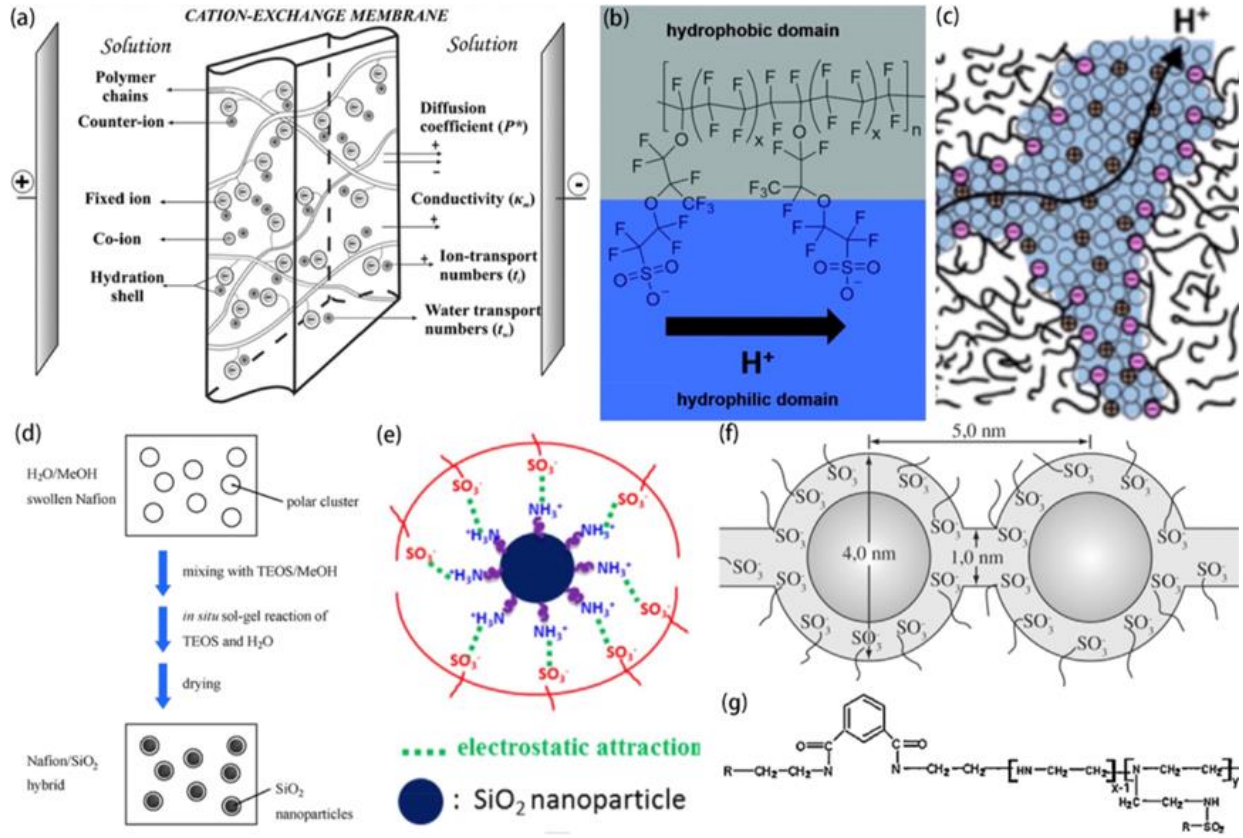

Figure 2. (a). Schematic diagram of an electromembrane system [13]; (b). Chemical composition [14] and (c). Proton conductive pathway of Nafion® [15]; Schematic preparation of (d). Nafion®/SiO_2 hybrid [10] and (e). Nafion®/amino-SiO_2 membrane [16]; (f). Cluster network model of hydrated Nafion® [10]; (g). Chemical composition of Nafion® membrane after interfacial polymerization of PEI cationic-layer [17].

2.2.3. Current research and interpretations

Electrodes can be categorized into two main types: 2D electrodes, which possess a flat and smooth plate-like structure, and 3D electrodes, characterized by their intricate and porous composition. Within the realm of 3D electrodes, there are three carbon-based varieties: carbon cloth, carbon paper, and carbon felt. In comparison to other 3D metal alternatives, carbon paper electrodes exhibit notably lower electrical resistivity [18]. However, carbon paper electrodes suffer from a constraint in the form of a limited reaction site, which in turn restricts the extent to which electrolyte molecules can come into contact with the electrode. Reducing the flow rate through the cell becomes essential due to the requirement for a substantial reaction area, which is crucial for the battery to efficiently undergo charging and discharging processes. Given the limited flow rate, the use of carbon paper electrodes isn't appropriate for specialized application needs. Graphite felt as electrode material brings the benefit of boosting localized turbulence, enhancing cell mixing, improving the efficiency of the system, with promoting electrolyte transportation within the entire system [18]. However, the limitations of graphite felt electrodes lie in their restricted wetting capability and the potential for degradation over prolonged operational durations.

In the VRFB system, the electrode is one of the most important components due to it can strongly affect the overall cycling stability of the system. To reduce the losses, the electrode should be well-designed. Developers have put much effort into minimizing the losses and fulfilling the design cues.

2.3. Memberane

2.3.1. Working principle

The cell membrane plays a pivotal part in the advancement of VRFB (*Fig. 2a*). Its primary function involves creating a barrier between cathodic and anodic electrolytes to prevent direct mixing. This

membrane exerts control over the efficiency, lifespan, and initial expenses of the VRFB. Simultaneously, it needs to facilitate the passage of specific ions, enabling the completion of redox reactions.

2.3.2. Membrane Design

An optimal membrane within the VRFB system would ideally exhibit robust thermal and chemical stability when exposed to strongly oxidizing vanadium electrolytes. Additionally, it should maintain a low rate of V ion crossover to achieve enhanced CE, EE, and prolonged operational longevity. Furthermore, the membrane should possess high proton conductivity to ensure improved VE [19]. The functionality of the cell hinges on two primary factors: thickness and pore size. Thinner membranes or larger pores have the potential to decrease area resistance (resulting in low Ohmic loss), but this could also lead to reduced ion selectivity. Analysis suggests that thinner membranes could excel in terms of maximizing EE at elevated current densities due to the shortened time for V ion diffusion. Conversely, thicker membranes or smaller pores manifest higher area resistance, directly affecting proton conductivity (VE), and causing pronounced polarization during charging and discharging, this configuration might perform better under lower current densities.

After everything is considered, two major parameters must be balanced to maximise the cell performance during the long cycling life.

VE pertains to the proton selectivity, and high VE is highly governed by the extent of proton permeation.

CE pertains to the disparity between the stored and released charge quantities and could be improved by reducing the V ion crossover effect across the membrane. EE is the outcome of the interplay between CE and VE, showcasing the effectiveness of energy conversion in extensive energy storage setups. Currently, striking the right balance between CE and VE proves exceedingly challenging, given that they often exhibit an inverse relationship across most materials. This equilibrium is typically dictated by the specific requirements of real-world applications.

1) Types of Exchange Membranes Based on Nafion

Currently, various membrane types are being explored in VRFB research: perfluorinated, partially fluorinated, and non-fluorinated membranes. Among these, the extensively utilized membranes are Nafion®, composed of perfluoro sulfonic acid polymers. Analysis and investigation have revealed that these hydrophilic sulfonic acid chains tend to aggregate, creating 4 nm channels that are embedded within a continuous fluorocarbon lattice (*Fig. 2b, c, f*) This structure facilitates the movement of ions while the hydrophobic backbones contribute to exceptional mechanical strength, capitalizing on their robust chemical/thermal stability and proton conductivity [10]. In addition to these advantages, untreated Nafion® membranes with prominent polar clusters still encountered a significant crossover of V ions, leading to potential reductions in CE and EE. To address these challenges, various modifications have been explored for Nafion® membranes, aiming to enhance either proton conductivity or diminish V ion permeability [10,16-17,20-21]. Hence, these pores can be filled by inorganic nanoparticles which can restrict the movement of larger V ions with comparatively larger stock radius [22], for instance, modifications like SiO_2 [10] and amino-SiO_2 [16] have been applied. SPEEK [20] or Daramic® [21] have been investigated. Furthermore, a repulsive polyethylenimine (PEI) layer has been employed on the membrane surface [17], these modifications and principles will be discussed briefly in the next section, although they all exhibited comparatively reduced V ion permeability and enhanced CE/EE, but need the sacrifice of the capital cost, or vice versa. Such as VANADion membrane [23] comprising an ultra-thin Nafion® layer and a cost-effective porous outer layer, has demonstrated slightly lower EE but with reduced costs. However, achieving an optimal balance among cost, proton conductivity, and V ion permeability remains a challenging goal for both current and future research endeavors.

2) Nafion-based Inorganic Hybrid Membranes

Currently, a prevailing approach to decrease V ion permeability involves employing inorganic nanoparticles (SiO_2) to occupy the polar clusters present on the exterior of Nafion®117 membrane (*Fig. 2d*). CE and EE were improved in 10 to 80 $mAcm^{-2}$. Notably, the superior EE achieved for both

membranes was 79.9% and 73.8% for Nafion®/SiO_2 and Nafion®117 under relatively low current density conditions, respectively. The cycling performance of the VRFB was also assessed, and the cell employing the Nafion®/SiO_2 membrane exhibited greater cycling stability while maintaining the initial CE and EE even after 100 cycles [10]. Regrettably, SiO_2 reduces electrical conductivity. To address the challenges of balancing ion selectivity and proton conductivity, Lin *et al.* [16] developed Nafion®/amino-SiO_2 using a modification of the SiO_2 incorporation technique (*Fig. 2e*). In this approach, amino-SiO_2 groups are integrated onto the Nafion membrane surface, effectively reducing the rate of V ion crossover. This reduction is achieved through electrostatic interactions between polar clusters and amino groups. Consequently, the Nafion®/amino-SiO_2 membrane has exhibited an even higher maximum EE (5.2% improvement) compared to pure Nafion® under low current densities [16].

3) Nafion Interfacial Polymerisation

An alternative approach to mitigate V ion permeability involves the lamination of polyethylenimine (PEI) onto the Nafion® surface (*Fig. 2g*) [17]. The growth of a repulsive layer has yielded notable results, with significantly improved maximum efficiencies at 50 $mAcm^{-2}$ (CE=96%, EE=85%) in comparison to the pristine Nafion® counterpart (CE=93.8%, EE=85%) [17], the improvement in cell performance and the enhanced selectivity for multi-valent V ions stem from the Donnan exclusion effect [17] which high-valent V ions are notably more challenging to be adsorbed compared to monovalent protons. In an attempt to address this, two distinct levels of interfacial polymerization were examined involving soaking Nafion® membrane in solutions with PEI concentrations of 2.5% and 5%. The findings indicated that the higher PEI concentration (resulting in a thicker cationic layer) effectively curtailed V ion crossover. However, it also led to a reduction in proton transfer rate, resulting in sluggish electrochemical performance (low VE) and decreased EE.

4) Nafion-based Polymeric Materials

One of the challenges to restricting the commercialization of VRFB is the high capital cost of the membranes, exchanging one or several parts of Nafion® with alternative skeleton material can greatly reduce the cost [24]. A less costly microporous polyethylene Daramic was recently studied and has been considered its suitability for VRFB membranes by B. Tian *et al.* [21], based on the special composition of mineral oils which is highly oxidation resistive and chemically stable, but high V ion permeability and thus low CE makes it unsuitable for VRFB operation [25], the possible improvements on ion selectivity are still required, the result after treatment of Daramic® material in 5 wt. % of Nafion solution was also summarized, which all modified Daramic /Nafion membranes exhibited lower V ion crossover and less water uptake in comparison with pristine Daramic membranes [21], and indicated the partial blockage of pores on Daramic membrane by embedded Nafion®. Another example developed by Luo *et al.* [20] to reduce the cost is to laminate an ultra-thin SPEEK layer with two outers recast Nafion®117 membranes, based on the low cost, good thermal /mechanical strength and highly resistive towards oxidative VO^{2+} ions. Upon investigation, a considerable decrease in V ion permeability can be noted. The variance in permeability between the Nafion® and N/S membranes could be attributed to their distinct nanostructures [26]. In contrast, the SPEEK backbone chain exhibits less hydrophobicity, and its sulfonic acid groups possess lower acidity. These attributes effectively hinder the formation of larger polar pores and clusters among adjacent dispersed sulfonic acid groups. Consequently, this leads to the creation of narrower ion exchange channels with more dead-ended branches. The cell efficiencies of the N/S membrane (CE=97.6%, VE=85.3%, EE=83.3%) were compared to those of the pristine Nafion® membrane (CE=93.8%, VE=90.7%, EE=85%) under moderate current densities. Cycling performance was also assessed, revealing no efficiency decay after 30 cycles. Although the N/S VRFB exhibited slightly lower EE compared to the Nafion® membrane, it is still regarded as a promising membrane for VRFB applications due to its affordability and robust cycling stability [20].

Another Nafion® hybrid membrane that has gained commercial popularity recently is VANADion [23], it is characterized by a dual-layer structure comprising a cost-effective, porous support layer that provides both high ionic conductivity and mechanical strength. This support layer is combined

with a dense Nafion® membrane (20 μm) that serves to filter out V ions, thereby minimizing self-discharge. Zhou *et al.* [23] compared the performance and efficiencies of VANADion and Nafion®115 membranes. They observed that the VANADion membrane exhibited an advantage with lower area resistance and higher VE. However, the CE of the VANADion membrane cell was only 88% at 80 $mAcm^{-2}$, while the pristine Nafion®115 achieved 95%. This discrepancy indicated that the V ion crossover resulted in significant self-discharge and capacity reduction due to the ultra-thin Nafion® layer in the VANADion membrane. Nonetheless, the CE of the VANADion membrane cell improved rapidly to satisfactory values of 94.6% and 95% under higher current densities of 240 and 320 $mAcm^{-2}$, respectively [23]. Moreover, the EE of the VANADion membrane is larger than Nafion®115 membrane in 120 $mAcm^{-2}$ or higher. This characteristic renders the VANADion membrane particularly promising for applications involving high current densities. Additionally, the investigation into capacity fading of the VRFB using these membranes revealed prior cycling stability for both VANADion and Nafion®115 membranes. Interestingly, the VANADion membrane has higher capacity fading compared to the Nafion®115 membrane (0.25% per cycle) under moderate current density conditions. The difference corresponds to the higher V ion crossover rates of the thinner VANADion membrane. Furthermore, a notable advantage of the VANADion membrane is its significantly lower capital cost. It is only 1/6th the cost of the Nafion®115 membrane due to the utilization of a mere 20 μm of expensive Nafion® material [23].

2.4. Bipolar Plate

2.4.1. Working principle

In large-scale VRFB applications, the system's output power is directly related to the quantity of unit cells connected in series. Bipolar plates (BPP) play a crucial role in these setups, as they serve to physically separate adjacent cells while also providing structural support and facilitating electrical connections [27]. Hence, there are several crucial characteristics of BPP including high electrical conductivity and mechanical/electrochemical stability [28], in order to obtain a longer lifespan.

2.4.2. Bipolar Plate Design

Practically, BPP can be categorized into three mainstreams: metal, graphite and polymer-carbon plates, metals offer the highest conductivity, but they are still unavailable to be applied in VRFB stack without a protective coating due to their chemical instability towards highly oxidative V ion electrolytes [29]. In comparison, carbon-based materials such as graphite possess excellent electrical conductivity, and chemical stability under acidic conditions, however, it also tends to be extremely expensive to handle due to its brittleness and suffering from electrolyte penetration through the porous structure [30], thus certain thickness is required to overcome the issue which brings extra weight, cost and volume. The composite carbon-polymer BPP is usually a good candidate for BPP material for VRB stack systems. Typically, the main conductive materials such as graphite and carbon black contribute around 80 wt%, the rest of the material is usually filled with flexural additives and binder polymers as the matrix [31]. Furthermore, the conductivity of the BPP material hinges on the quantity of conductive particles and their interconnections within the insulator matrix framework.

2.4.3. Current Research and Interpretation

Zhang *et al.* [32] discovered that the conductivity of the BPP is directly proportional to the number of fillers, for example, carbon black or carbon fibres, incorporated into the 3D framework, whereas Haddadi *et al.* [33] demonstrated an inverse correlation between the quantity of carbon black and conductivity. In the case of composite material, electrical resistance was significantly elevated when carbon black content fell below 5 wt%, and then exhibited a rapid increase up to 25 wt%. The most optimal content of carbon black in the graphite/carbon black composite was determined to be 15 wt%, striking a better balance between conductivity and mechanical stability, particularly under highly acidic conditions [30]. The quantity of carbon black is tightly regulated due to the potential formation of pores and aggregates, which occurs when the content is either too low or too high, respectively. However, replacing a certain amount of carbon black with carbon fibers or carbon nanotubes (CNTs)

can further enhance the conductivity due to better connection by conductive particles within the matrix could be established [29]. Unfortunately, Parker *et al.* [31] discovered that the carbon content within the composite BPP cannot be excessively high or low. When the content exceeds 90 wt%, the compression-molded material becomes exceedingly fragile and brittle. Conversely, if the content falls below 60 wt%, the plate's processibility is hindered due to the excessively high viscosity of the material.

Recently, graphite/CNTs filled polyphenylene (PPS) BPP was fabricated by Caglar *et al.* [29] via injection molding, in this particular scenario, graphite and a titanate coupling agent were incorporated as the primary conductive material and flexural additive within the matrix of CNTs. This integration aimed to ensure favorable mechanical strength and the smooth flow of conductive particles. Consequently, the conductivity of the BPP increased from 6.4 to 57.3 Scm^{-1} compared to the sample lacking these additives.

As mentioned previously, some particular coated metals can be applied as good BPP as well, Han *et al.* [34] have developed an IrOx-coated TiO_2 nanotubes BPP. The application of an IrOx coating is believed to effectively decrease electron transfer resistance due to its catalytic properties. This enhancement resulted in a cell efficiency that was 3-4% higher than its graphite counterpart. Moreover, the BPP demonstrated robust cycling stability over 100 cycles. Notably, the metal-based BPP exhibited substantial improvements in electrocatalytic performance, chemical stability, and a reduction in charge transfer resistance.[35]

3. Environmental Impact and Solutions

3.1. Impacts

VRFB has larger environmental impacts than others. This discrepancy can be primarily attributed to the inclusion of vanadium pentoxide and tetrafluoroethylene [35]. Vanadium Pentoxide is derived through various processing routes. In some scenarios, it is a by-product of steel production, specifically obtained from methods involving blast furnaces consuming hard coals or electric arc furnaces. In other scenarios, V_2O_5 is produced from residues resulting from crude oil burning [35]. Therefore, unlike other batteries, the production process of vanadium pentoxide used for the electrolyte causes significant carbon emissions.

Additionally, the environmental concerns linked to tetrafluoroethylene (TEF) in the Nafion® membrane's production are rooted in the intricate and intricate synthesis processes it requires [35]. The production of Nafion® requires fluorination and sulfonation, utilizing high-impact polymers like tetrafluoroethylene. These processes contribute to a significant environmental impact, including ozone depletion potential. Tetrafluoroethylene plays a crucial role in the manufacturing of Nafion®. It stands as the dominant membrane material utilized in VRFB due to its unique properties. The incorporation of tetrafluoroethylene into the synthesis process imparts essential traits to the Nafion® membrane, rendering it well-suited for its application in flow batteries. Despite the exploration of alternative membrane materials, Nafion® remains a prevalent choice, and the production of this membrane inherently involves the utilization of tetrafluoroethylene.

3.2. Solution

3.2.1. Solutions in industrial process

Substituting the Nafion® membrane with an alternative material can serve as an alternative approach to mitigating the environmental concerns highlighted earlier, rN212/GO offers a possible alternative to Nafion®. The rN212/GO has lower production costs and improved permeability. This is due to the fact that membrane cost is determined by its thickness, and relatively thinner rN212/GO is more cost-effective than Nafion®. Additionally, the inclusion of graphene oxide (GO) makes permeation more difficult in rN212/GO compared to regular Nafion® material.

3.2.2. Solutions beyond industrial process

When assembling the battery, incorporating a safeguarding layer around it proves to be an efficient measure for mitigating the potential leakage risks. Introducing a protective coating using vegetable oil-based polyurethane during the construction of VRFB yields significant benefits. This specific coating type demonstrates steadfastness in conditions below 180 °C, thus assuring its durability and resilience against premature degradation. Another notable advantage lies in the relatively economical application cost of polyurethane coatings. Moreover, the absence of the necessity to include harmful elements such as fluorides renders this polyurethane coating ecologically sustainable [36].

Besides this, integration of the temperature regulation system can serve as a preventive measure against elevated temperatures that could result in the precipitation of V_2O_5. The hydrated complex $[VO_2(H_2O)_3]^+$ remains chemically stable under 330K, but transformation into H_3VO_4 via deprotonation followed by a condensation precipitation of V_2O_5 might occur if temperature increases. The solid-state precipitate might lead to internal obstruction and have the potential for membrane damage [7].

4. Conclusion

VRFB offers a promising avenue for efficient energy storage. This article delves into the intricate aspects of VRFB technology, exploring electrode functionality, membrane design, and bipolar plate considerations. The significance of Nafion® membranes in VRFBs is highlighted, along with the environmental concerns associated with their production. Several innovative strategies to address these environmental issues have been identified, ranging from alternative membrane materials to protective coatings. As research continues to push the boundaries of VRFB technology, optimizing efficiency and reducing environmental impact are paramount. VRFBs, with their distinctive capability to store substantial amounts of energy, exhibit the potential to revolutionize the energy landscape, provided they evolve in a sustainable and environmentally responsible manner. By embracing both technological advancements and ecological consciousness, VRFBs can contribute to a greener and more sustainable energy future.

Authors Contribution

All the authors contributed equally and their names were listed in alphabetical order.

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