

# Comprehensive Analysis of Critical Issues in All-Vanadium Redox Flow Battery

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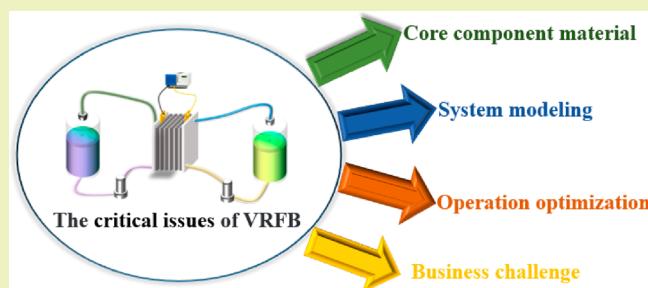
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**ABSTRACT:** Vanadium redox flow batteries (VRFBs) can effectively solve the intermittent renewable energy issues and gradually become the most attractive candidate for large-scale stationary energy storage. However, their low energy density and high cost still bring challenges to the widespread use of VRFBs. For this reason, performance improvement and cost reduction of VRFBs are the keys to their commercialization and large-scale energy storage applications. On the basis of this, this perspective briefly describes the development status of renewable energy and energy storage technology and summarizes the existing bottlenecks that affect the development of VRFBs. Meanwhile, the critical technologies of VRFBs are reviewed, and the research progress in recent years and the challenges that need to be overcome are introduced. This perspective focuses on four aspects, including core component material, system modeling, optimization operations, and future business challenges. Then, a comprehensive analysis of critical issues and solutions for VRFB development are discussed, which can effectively guide battery performance optimization and innovation. The views in this perspective are expected to provide effective and extensive understanding of the current research and future development of vanadium redox flow batteries.

**KEYWORDS:** Vanadium redox flow battery, Component material, System modeling, Optimization operation, Business challenge



## INTRODUCTION

In recent years, as the global “carbon peak” and “carbon neutral” goals have been proposed, the demand and utilization of wind energy and photovoltaic (PV) renewable energy have received particular attention.<sup>1</sup> It is worth pointing out that the large-scale integration of random and intermittent renewable energy sources will greatly undermine the stability of the grid system.<sup>2–4</sup> Therefore, it is necessary to configure a suitable energy storage system on the power generation side and the user side to stabilize the intermittence and fill the gap between power generation and load.<sup>5–7</sup>

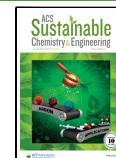
Currently, the technologies that can be used for large-scale energy storage include physical energy storage through the pumped hydro system (PHS), compressed air energy system (CAES) and flywheel energy system (FES), electromagnetic energy storage through superconducting magnetic energy storage (SMES) and supercapacitors (SC), chemical energy storage through fuel cells (FC) and batteries, and thermal energy storage (TES) by heating or melting materials.<sup>8–11</sup> Figure 1 gives an analysis of energy storage technologies that can be integrated on a large scale. As of the end of 2020, the cumulative installed capacity of energy storage projects in operation worldwide reached 191.1 GW, of which the cumulative installed capacity of pumped storage was the largest, accounting for 90.3%.<sup>12–14</sup> Meanwhile, the installed capacity of electro-

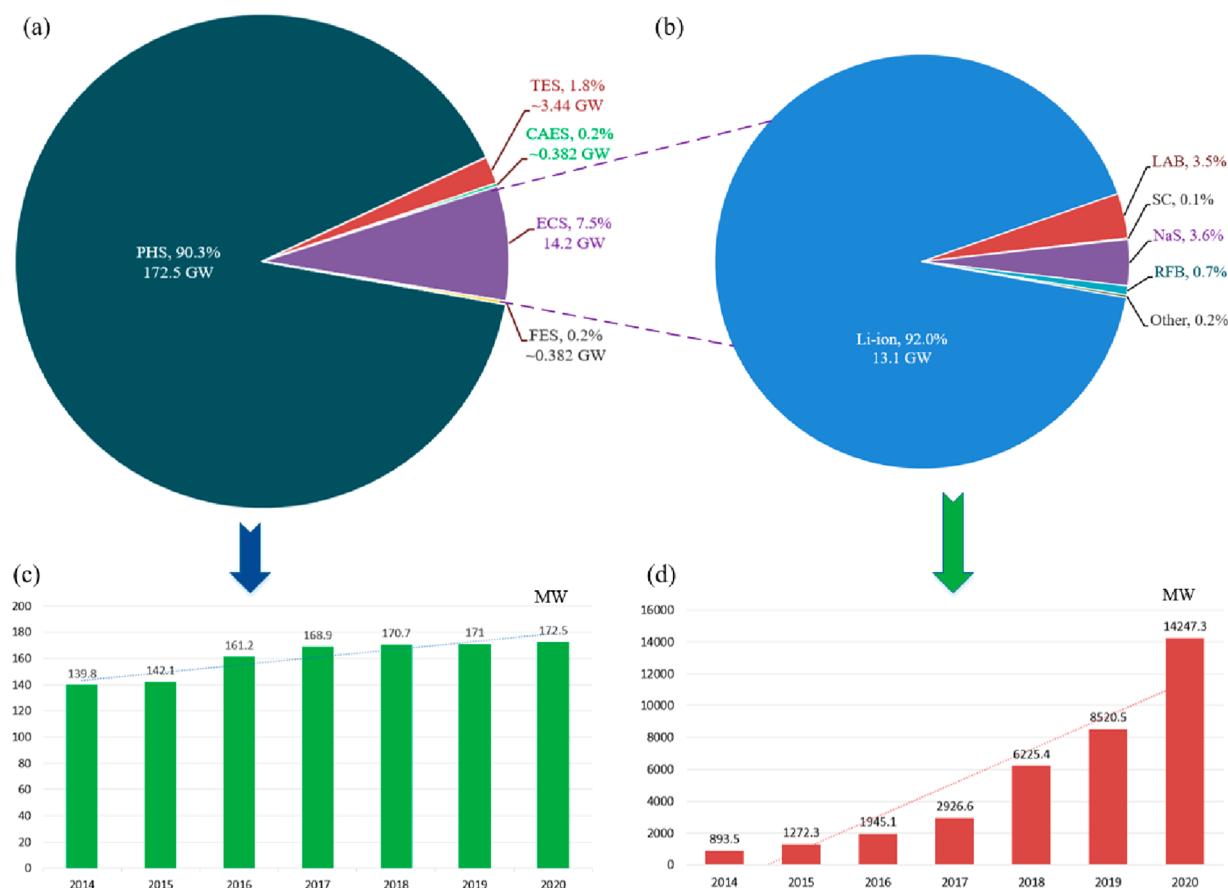
chemical energy storage (ECS) followed closely behind, accounting for 7.5%, and this information is shown in Figure 1a and b. Additionally, physical energy storage has the characteristics of mature technology and is large scale. It is mainly realized in the mutual conversion of electrical energy and mechanical energy.<sup>15,16</sup> For the ECS, it has become currently the most widely used energy storage technology with the greatest development potential, including lithium-ion batteries (Li-ion), lead-acid batteries (LAB), sodium–sulfur batteries (NaS), and redox flow battery (RFB) energy storage technologies.<sup>17–20</sup> To be specific, as of the end of 2020, the cumulative installed capacity of ECS reached 14.2 GW, a year-on-year increase of 49.6%. As shown in Figure 1d, the key conclusion can be inferred that ECS is becoming more and more important.<sup>21,22</sup> In contrast, although the scale of PHS is huge, it is restricted by the geographical environment and has grown slowly this year, as shown in Figure 1c. Similarly, the scale of CAES is also large, while it is affected by the geographical environment and

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**Figure 1.** Statistics of global energy storage distribution: (a) global energy storage layout, (b) ECS capacity distribution, (c) installed statistics of PHS, and (d) ECS installed capacity.

geological conditions, and the equipment needs strong pressure-bearing capacity.<sup>23</sup> FES can be used to smooth the power of renewable energy, but it has serious self-discharge, poor safety, high cost, and requires a vacuum environment, which makes it not suitable for large-scale long-term storage.<sup>24</sup> Furthermore, the TES can be applied to special occasions, but its self-discharge is serious and application scenarios are few.<sup>25</sup> SMES and SC have serious self-discharge and high cost and are not suitable for long-term energy storage.<sup>26–28</sup> In terms of ECS, laboratories are cost effective, but it has serious self-discharge and a short lifespan.<sup>29–31</sup> The NaS has high energy density and efficiency, but it requires a high-temperature working environment, so there is a safety hazard.<sup>32–34</sup> Li-ions are the best choice for energy storage in terms of efficiency, specific energy, and lifespan. However, lithium resources are becoming scarce, and Li-ions mainly serve for terminal consumption. Therefore, cost-effective high cost and low security make it unsuitable for large-scale stationary energy storage.<sup>35</sup> Considering factors such as safety, life, environment, efficiency, and more, RFBs are the preferred technology for large-scale energy storage applications.<sup>36–38</sup>

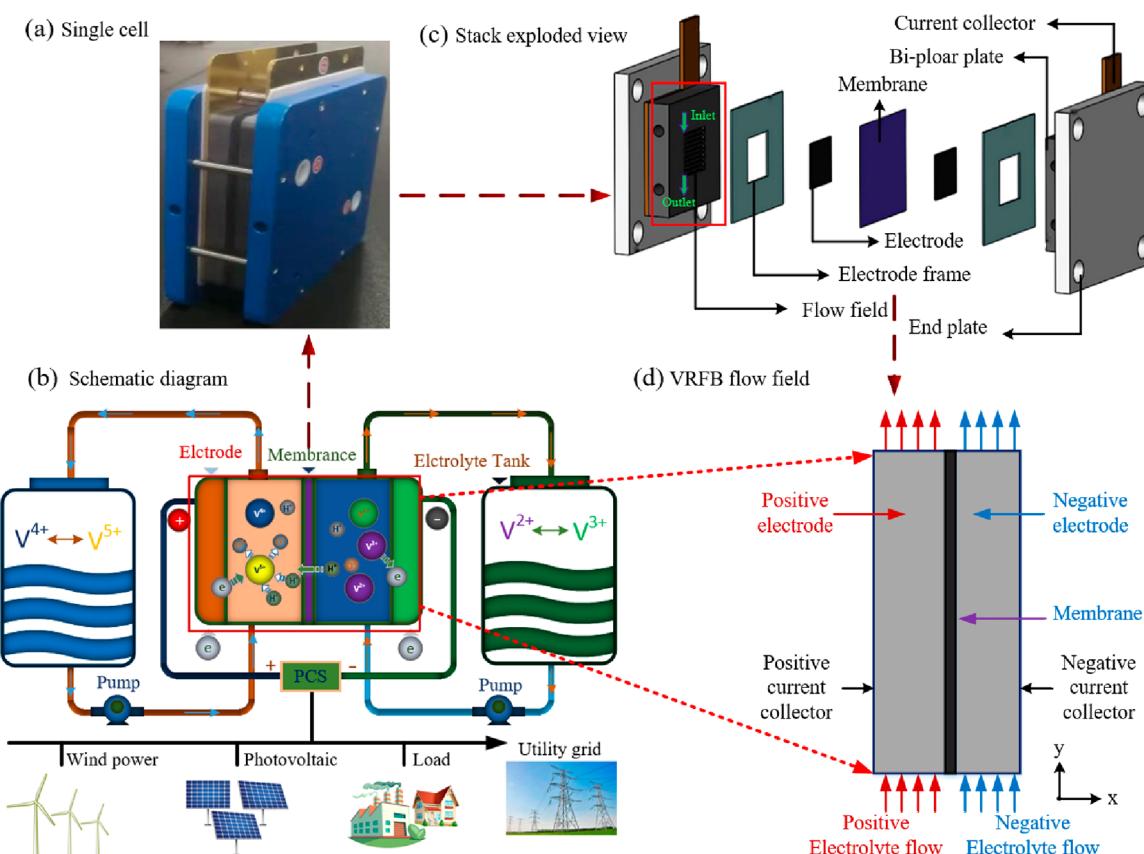
Compared with other RFB technologies, the powers and capacities of VRFBs are designed independently of each other. It has the advantages of easy expansion, high safety, no cross-contamination, long service life, flexible design, environmental friendliness, and cost effectiveness, which meet the conditions well for large-scale energy storage applications.<sup>39</sup> In the past few decades, continuous innovations have been made on VRFB materials, and battery performance has been greatly improved.

Regrettably, the costs of VRFBs are still at a relatively high level, and the low energy density factors limit the large-scale applications of VRFBs in the field of energy storage.<sup>40</sup> The theoretical energy density of a vanadium redox battery reaches 50 Wh kg<sup>-1</sup>, and the actual energy density is only about 35 Wh kg<sup>-1</sup> due to factors such as battery polarization and mass transfer delay.<sup>41</sup> Therefore, improving the performances of VRFBs and reducing the system cost are critical issues in the research.

At present, VRFB technology is not yet fully mature, and there are many problems in the process of industrial development. The main contribution of this perspective is to analyze and discuss the critical issues of battery development in terms of the analysis of renewable energy power generation and energy storage technology, including the basic theoretical research of VRFBs, the development of key materials, advanced modeling methods, battery operation optimization, and development and challenges. This perspective clarifies the factors affecting the performance and application of VRFBs, which is providing references and suggestions for future VRFB research.

## OVERVIEW OF VANADIUM REDOX FLOW BATTERY

**Working Principle.** It is well known that typical VRFBs typically consist of the stack (power modules), electrolytes and tank (energy modules), circular pumps and pipeline systems (mass transfer modules), and power electronics (transform devices). To illustrate the operating mechanism of VRFBs, Figure 2 shows a schematic diagram of the working principle of a VRFB cell.<sup>42</sup> The stack is a core component of VRFB, providing an electrochemical reaction place, achieving electrical energy



**Figure 2.** Schematic diagram of vanadium redox flow battery: (a) single cell, (b) schematic diagram of a single cell, (c) stack exploded view, and (d) vanadium redox flow battery flow field.

and chemical mutual conversion. Moreover, the performance of electric rectification determines the electrochemical performance, cost, life, and maintenance of the battery.<sup>43</sup> With such advantages of good safety, long cycle life, and independent design of power and capacity, VRFBs play positive roles in the consumption of renewable energy and improve the peak and frequency regulation of the power grid and the reliability of the power supply and more.

The flow field is the site of the electrochemical reactions of VRFBs, as shown in Figure 2d, which is mainly composed of an electrode frame, electrode, membrane, and bipolar plate (BPP). It needs to be emphasized that the design of the flow field directly determines the transmission characteristics of the electrolyte, which affect the liquid phase mass transfer and electrochemical reaction process of the electrode surface, and ultimately affects the overall performance of the battery. Besides, the electrolyte in the flow field mainly causes concentration polarization.<sup>44,45</sup> The concentration polarization expression is

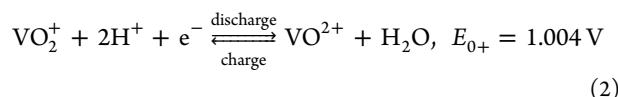
$$\eta_{con} = \eta_{con}^+ + \eta_{con}^- \\ = \frac{RT}{zF} \ln \left( 1 - \frac{i}{zFk_m c_r^+} \right) + \frac{RT}{zF} \ln \left( 1 - \frac{i}{zFk_m c_r^-} \right) \quad (1)$$

where  $\eta_{con}$  is the concentration polarization, V, and  $c_r^+$  and  $c_r^-$  are the reactant concentrations, mol L<sup>-1</sup>. Here,  $i$  is the current density, mA cm<sup>2</sup>,  $k_m$  the mass transfer coefficient, m s<sup>-1</sup>,  $F$  the Faraday constant, 96,485 C mol<sup>-1</sup>, and  $R$  the molar gas constant, J mol<sup>-1</sup> K<sup>-1</sup>.

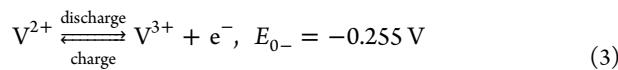
**Electrochemistry of VRFB.**  $\text{VO}_2^+$ / $\text{VO}_2^+$  is stored in the positive electrode tank, and  $\text{V}^{2+}/\text{V}^{3+}$  is stored in the negative

electrode tank. During the operation of the battery, the valence states of vanadium ions in the tank change. The electrochemical reactions generated by the VRFB positive and negative electrodes are shown in eqs 2 and 3. The total reaction is shown in eq 4, and each half-reaction gives off an electron. The standard battery difference of the battery is 1.259 V.<sup>46</sup>

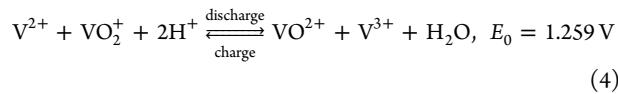
Positive reaction:



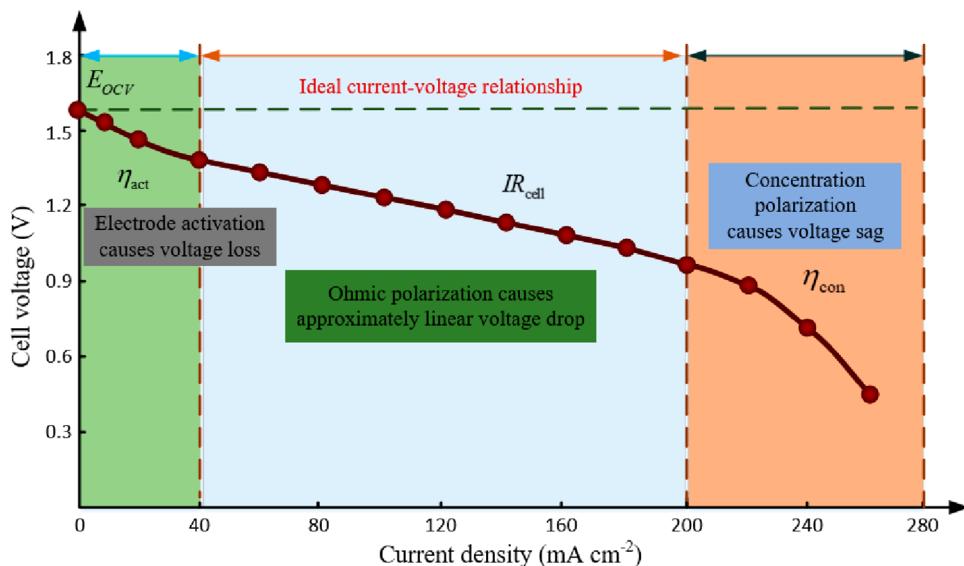
Negative reaction:



Overall response:



**VRFB Charge and Discharge Process.** The voltage of the battery consists of an open circuit voltage (OCV), ohmic polarization ( $I_{Rcell}$ ), activation polarization ( $\eta_{act}$ ), and concentration polarization ( $\eta_{con}$ ), as shown in eq 5. The ohmic polarization is the product of the current and the internal resistance of the cell.<sup>47</sup>



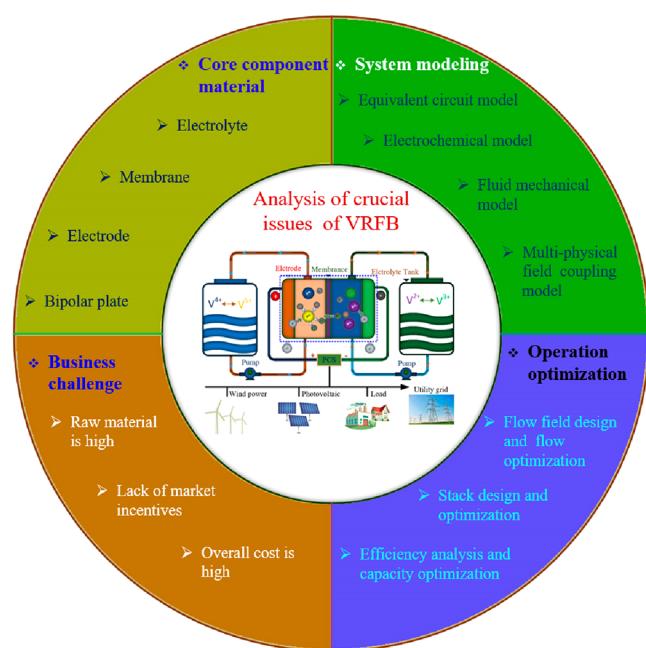
**Figure 3.** VRFB discharge curve and polarization phenomenon.

$$E_{cell} = E_{OCV} + IR_{cell} + \eta_{act} + \eta_{con} \quad (5)$$

In the composition of the battery voltage, the OCV occupies the main part and is affected by the nature of the battery bipolar system, the nature of the material, the composition and concentration of the solution, the temperature, the state of the electrode interface, and other factors. Meanwhile, the ohm polarization occurs instantaneously due to the polarization caused by the electrolyte, electrode material, diaphragm resistance, and contact resistance between various components. In terms of activation polarization, it occurs when the electrochemical reaction rates of active substances in positive and negative electrodes are less than that of the electron movement rate, and the response time is faster. In addition, the concentration polarization is the phenomenon where the electrode potential deviates from the equilibrium potential when the ionic concentration of the electrode interface layer is different from that of the body solution. As shown in Figure 3, different battery polarizations occurred at different current densities. To this end, in the charge and discharge processes, how to reduce the battery polarization and improve the battery efficiency are also the focus of VRFB research.<sup>48</sup>

**Analysis of Critical Issues of Vanadium Redox Flow Batteries.** VRFBs are the most concerned and prominent RFBs currently developed because of their outstanding advantages. However, VRFBs also have several problems. For example, the low electrolyte solubility will result in low energy density, and the porosity of the electrode may reduce the polarization and energy efficiency (EE) of the battery. Besides, the design of the flow field structure will increase the mass transfer resistance, and membrane selectivity may cause ion crossover and electrolyte imbalance. Then, the modeling accuracy problem leads to inaccurate estimations of performance parameters, which lead to degradation of the battery performance. The stack layout causes transmission delay and concentration polarization. The optimal acquisition of EE and system efficiency (SE) and high costs constrain battery applications.<sup>49,50</sup> The above problems will seriously restrict the development of VRFBs. Another thing to be stressed is that there are also engineering problems with VRFBs that can affect battery core performance, such as electrochemical degradation of components, electrolyte leakage,

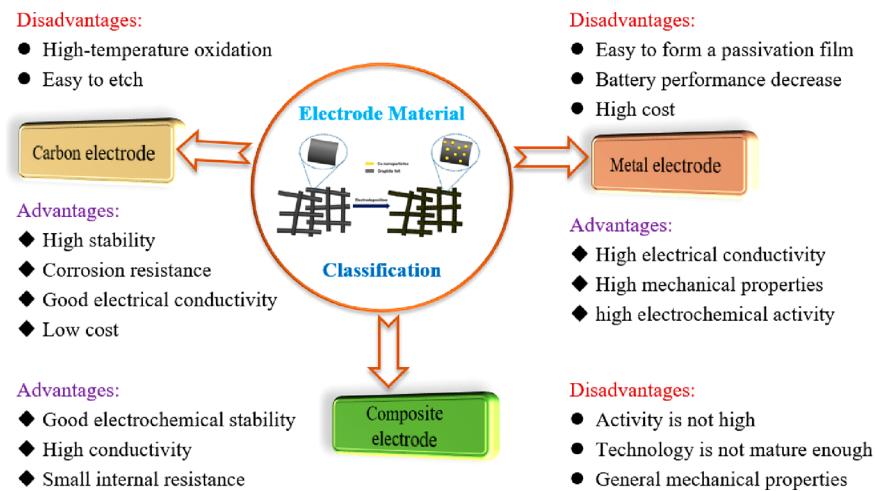
and mechanical failure of critical components.<sup>51</sup> Combined with the above descriptions, Figure 4 shows a summary of the key



**Figure 4.** Analysis and summary of crucial issues of VRFB.

issues that hinder the development and application of VRFBs. At the same time, based on the research status of VRFB, the above problems are summarized into four crucial issues:

- (i) Core component materials, including electrolyte, ion conduction membrane, electrode, BPP, and more. Component materials determine fundamentally the basic battery properties. The solubility of the electrolyte determines the energy density, and the stability determines the safety of the battery. For instance, the membrane selectively blocks the crossover of vanadium ions, reduces the occurrence of side reactions, and maintains the balance of electrolytes.<sup>52</sup> Then, the electrode activity and porosity determine the polarization



**Figure 5.** Electrode material classification and characteristic analysis.

degree of the battery. The material's internal resistance directly affects the ohmic overpotential of the cell. In addition to these, the BPP directly affects the conductivity of the cell.

- (ii) System modeling, including common equivalent circuit models and electrochemical models. Taking into account the complexity of the flow battery, a single modeling method cannot effectively obtain the physical parameters and comprehensively characterize the battery performance. Therefore, the multiphysical field coupling model of electrical, chemical, and kinetic fields has stood out recently to solve the accuracy issues. For this purpose, the multiphysical field model is also the development trend of VRFB modeling.
- (iii) Operation optimization. Over recent years, the performances of VRFBs have been improved gradually without the research and development of new materials, which should be attributed to a variety of operation optimization methods for VRFBs. Their methods commonly used include flow field design, flow rate optimization, high-performance stack development, EE analysis, and capacity optimization.
- (iv) Commercial challenge. Due to the high price of raw materials, the costs of VRFBs are high. At present, VRFBs are in the initial stage of commercialization from the demonstration project and lacks a series of market incentive mechanisms, which is not conducive to promotion of the batteries. Meanwhile, how to reduce the costs of VRFBs is also one of the important issues in studying VRFBs.<sup>53</sup> Given these challenges, this perspective analyzes and summarizes the crucial issues of VRFBs comprehensively for the first time, which is of great significance to the development of VRFBs.

## KEY COMPONENT MATERIALS

It is well known that the improvement in the performances of VRFBs is inseparable from the optimization improvements of key materials in the battery structure. This is because the electrolyte solution of the battery, ion exchange membrane, and electrodes that provide electrochemical reaction venues determine battery energy storage capacity, power density, and EE.<sup>54</sup> To improve the overall performance of the battery,

researchers are constantly trying to find better-performing key materials for VRFBs and modify the key materials.

**Electrode.** The electrode is the core assembly of the battery power unit. As it provides an electrochemical reaction site, the electrode directly affects the battery polarization (activation polarization, ohmic polarization, and concentration), which in turn affects the performance and cost of the battery. According to existing research, the electrodes of high-performance VRFBs should have the following characteristics, including (i) high activity and effectively reducing activation polarization, (ii) high porosity, which is helpful for effective electrolyte transfer, reduction in concentration polarization, and pump loss; (iii) strong electrical conductivity, which reduces ohm polarization. Therefore, materials that have high porosity, strong conductivity, and good activity are the keys to improving the operating capabilities of VRFBs. At present, the commercial electrodes of VRFBs mainly include carbon electrodes, metal electrodes, and composite electrodes. Figure 5 shows a classification of electrode materials of VRFBs and analyzes the characteristics of three different electrode materials.<sup>55,56</sup>

In recent years, the research of electrodes mainly focuses on the stabilities of electrode materials, catalytic activities, porosities, resistances, side reactions, and costs and has achieved remarkable results. It is worth noting that electrode compression is also an effective way to improve the performances of VRFBs. On the basis of these findings, Gonzalez et al.<sup>57</sup> prepared carbon nanowall thin films as VRFB cathode materials, and cyclic voltammetry showed that a battery with this electrode had low overpotential and excellent electrochemical performance. Oh et al.<sup>58</sup> conducted a numerical study on the compression effect of carbon felt electrodes in VRFBs, and the results showed that voltage compression could improve the conductivity of the battery and reduce the ohmic polarization of the electrode. In addition, a reasonable electrode compression ratio would not significantly change the kinetics of electrochemical reactions and the migration of active substances. Blanco et al.<sup>59</sup> used graphene-modified graphite felt as an electrode for VRFBs, and the results showed that the electrode improved the electrochemical activity and dynamic reversibility of the battery through cyclic voltammetry impedance spectroscopy and charge/discharge experiments. Wang et al.<sup>60</sup> proposed a nonuniform model considering the electrode shape deformation and nonuniformity of physical properties. The invasion ratio of local porosity and the morphology of the electrode were studied, and the

heterogeneous compression electrodes with different local porosities and permeabilities were obtained. The experimental results show that the optimized compression ratio is 55.7%, and the concentration uniformity, current density, and overpotential are minimized. Ghimire et al.<sup>61</sup> found that thermal oxidation of graphite felt in the air is the most extensive electrode activation method to improve the performances of VRFBs. Thermal oxidation was closely related to material loss rate, and the best performance of the electrode was observed at 750 °C for 5 min. Deng et al.<sup>62</sup> proposed a new composite electrode to overcome the contradiction between high graphitization and uniform heteroatom doping. The composite electrode achieved fast charge transfer and high electrocatalytic activity, enhancing the redox reaction, and it had high stability and high efficiency under high current density. Abbas et al.<sup>63</sup> studied the effect of electrode porosity on the charge transfers of VRFBs. The porous activated carbon developed from biomass waste was charged and discharged. The results show that the customized porosity has a significant effect on charge migration and improves VRFB performance. Yadav et al.<sup>64</sup> proposed a preparation method of electrospinning with fibers possessing a ribbon-like cross-sectional shape to manufacture electrodes, studied various physical and transmission characteristics of the electrode, and compared it with Freudenberg H23 carbon paper; the results show that the ribbon-based electrode had better performance and power density. Kwon et al.<sup>65</sup> applied benzoyl peroxide (BPO) to a VRFB with a carbon felt electrode and demonstrated an excellent 75% EE at a current density of 100 mA cm<sup>-2</sup>, suggesting that BPO has a strong electrocatalytic effect on the surface.

To sum up, electrode research mainly focuses on the performances and costs of electrode materials. The electrode should have good chemical stability, reaction activity, specific surface area, porosity, internal resistance, and side reactions to ensure that the electrode is resistant to strong acid and oxidation and has high reversibility, a large reaction area, small polarization, low side reaction, and low cost.

**Electrolyte.** The electrolyte is a VRFB energy storage carrier and has a significant impact on the overall performance and cost of the battery.<sup>66</sup> It is understood that in large-scale energy storage, the electrolyte accounts for about 50% of the total cost of the battery. However, the promotion and application of VRFBs are seriously restricted in recent years because the cost of raw material ( $V_2O_5$ ) is high.<sup>67</sup> According to existing research, the energy densities of VRFBs mainly depend on the solubility of the electrolyte. The current solubility is 1.6–2.0 M, and how to enhance the solubility to improve the energy density is a research hotspot in the field of RFBs. For the study of electrolytes, the initial research only focuses on the composition and temperature characteristics of the electrolyte. With the continuous progress of electrolyte technologies, the current electrolyte studies are mainly to increase solubility and stability. In other words, the existing scholars are committed to promoting the battery energy density by increasing the solubility and increasing the stability of the electrolyte by adding additives.<sup>68</sup> In addition, vanadium ions in different valence states of electrolyte solution show significantly different colors, which can avoid cross-contamination of the positive and negative electrolyte active substances to extend the cycle life of the battery. The changes in vanadium ions and potential in different valence states are shown in Figure 6.

The electrolyte is an important part that affects the electrochemical performance of VRFBs. In recent years, a lot

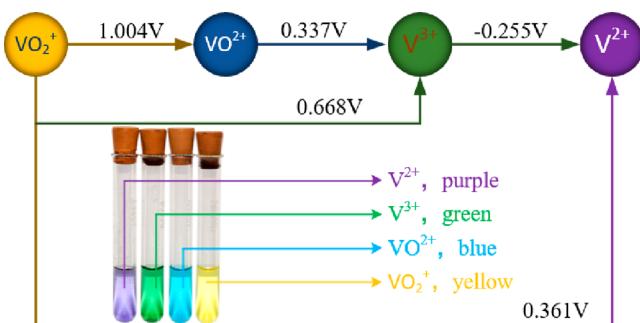
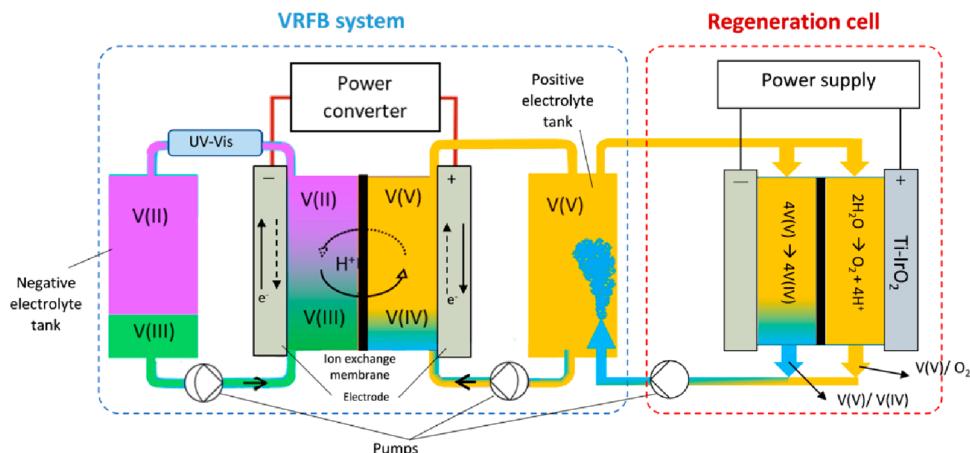


Figure 6. Different vanadium samples showing color valence changes and electrode potentials.

of researches have been explored to improve the stabilities and electrochemical activities of electrolytes, and a series of achievements have been made. Specifically, Wang et al.<sup>69</sup> used several acid compounds as additives in a V(V) electrolyte to improve the stability of a V(V) electrolyte in a certain temperature range. Subsequently, the cyclic voltammetry steady-state polarization method and electrochemical impedance spectroscopy were used to prove that the addition of additives improved the electrochemical behavior of the V(V) electrolyte. Zhang et al.<sup>70</sup> mixed positive and negative electrolytes, which was limited by the average price of the mixed electrolyte, but could prolong the cycle life of the battery and alleviate the discharge capacity attenuation. Cecchetti et al.<sup>71</sup> found that cross-contamination of vanadium led to the reduction of Coulomb efficiency (CE) and the loss of electrolyte imbalance and mainly affected the negative electrolyte. Yang et al.<sup>72</sup> studied the viscosities and conductivities of sulfate-chloride electrolytes. Electrochemical tests found that electrolytes with 2.2 M vanadium concentration, 2.75 M sulfate concentration, and 5.8 M chloride ion concentration had the best electrochemical performance due to the combined influence of viscosity, conductivity, and active vanadium ion concentration. Jirabovornwisut et al.<sup>73</sup> believed that the biggest factor of battery capacity loss was electrolyte imbalance. Besides, the cause, influence, measurement, and regeneration of electrolyte imbalance were also analyzed and discussed, which can improve the operation and manufacture of VRFBs. Murugesan et al.<sup>74</sup> designed an optimal VRFB electrolyte by introducing competing cations and bonding anions to regulate the vanadium electrolyte, considering that the operational stability of the electrolyte seriously affects the VRFB performance. The results showed that the operating temperature range of the battery increased by 180%, and the energy density increased by 30%. Poli et al.<sup>75</sup> proposed a novel electrolyte rebalancing approach for VRFBs by counterbalancing the charge imbalance caused by hydrogen and oxygen evolution. A specially designed regeneration system was used, and the electrolyte imbalance was greatly reduced through testing, proving that the balancing process was successful (Figure 7). Shin et al.<sup>76</sup> controlled the composition of the initial anode and cathode electrolytes, which could effectively suppress the diffusion of water cross flux between the positive and negative electrodes and ultimately alleviate electrolyte imbalance. Zhang et al.<sup>77</sup> used chloride ions as an electrolyte additive for VRFBs. The results showed that the chloride ion improved the reactivity of  $VO^{2+}/VO_2^+$ , and the low cost of the chloride ion provided a broad prospect for the application of high-performance VRFBs. Kim et al.<sup>78</sup> investigated methanesulfonic acid (MSA) as an additive to improve the thermal stabilities and

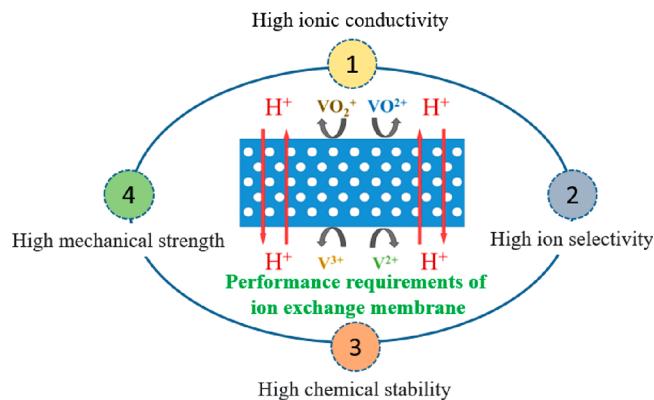


**Figure 7.** Novel electrolyte rebalancing method for vanadium redox flow batteries. [Reproduced with permission from ref 75. Copyright 2021, Elsevier.]

electrochemical performances of VRFB electrolytes. MSA delayed the precipitation of vanadium, enhanced the diffusion of V(III) and V(IV) ions, and improved the redox reaction rate of V ions. To sum up, the MSA electrolyte improves the electrolyte utilization rate, EE, and energy density.

At the same time, the capacities of VRFBs are determined by the volume and solubility of the electrolyte. Therefore, the electrolyte stability directly affects the performance of the battery. Nevertheless, the electrolyte is an aqueous solution system, and the solubility of ions is limited. For this reason, how to improve the electrolyte system to improve the concentrations and stabilities of ions in solution is the focus of electrolyte research. Referring to existing VRFB electrolyte studies, the electrolyte preparation process should be improved, focus on the optimization process, prevent electrolyte imbalance, and avoid electrolyte leakage. In terms of battery capacity attenuation and regeneration, more strategies (e.g., add additives) should be found to deepen the discharge capacity attenuations and maintain the stabilities and electrochemical activities of electrolytes. In the vanadium ion concentration of the active substance, it is necessary to find suitable methods to improve the solubilities of vanadium ions in the electrolyte.

**Membranes.** Membranes are used to separate positive and negative electrodes and to conduct hydrogen ions. Commonly used membrane materials include the Nafion membrane and Daramic membrane.<sup>79</sup> The membrane is not only an isolation material to block the electrolytes of positive and negative electrodes and prevent cross-contamination but also plays a role in mass transfer, making hydrogen ions move through the diaphragm to maintain electrolyte balance.<sup>80</sup> In the VRFB, the membrane should have a higher ion exchange capacity, a higher electrical conductivity, good chemical and thermal stabilities, lower swelling ratios, lower surface resistance, lower vanadium ion penetration, water migration, and lower cost.<sup>81</sup> Therefore, it is required that the membrane material has the characteristics of strong oxidation resistance and high stability. The membrane accounts for a significant ratio of the total cost of the system, and the performance of the battery is significant. To solve these challenges, the current studies of membranes are mainly concentrated on high-performance membranes with high electrical conductivities, low permeabilities, chemical properties, and stable mechanical properties.<sup>82</sup> To sum up, the ideal ion exchange membrane should have the performance characteristics as shown in Figure 8.<sup>83</sup> In addition, the availability of raw



**Figure 8.** Performance requirement analysis of ion exchange membrane.

materials, operability, and rationality of the membrane-making process are the key factors for the commercial use of VRFB ionic conductive membranes, and also important aspects to be considered in the future development of VRFB ionic conductive membranes.

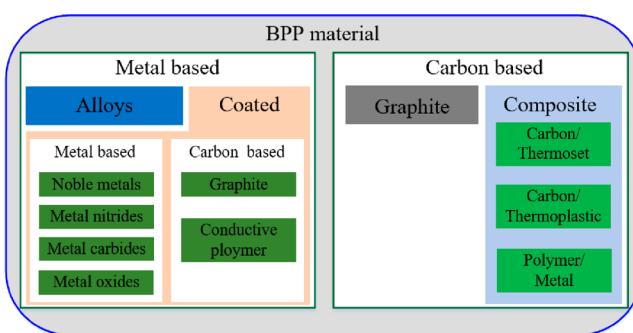
The membrane is one of the key components of VRFBs, which not only affects the whole cycle performance but also determines the economic feasibility of the system. The performance improvement of the membrane has been the focus of VRFB research in recent years. Many scholars have studied membrane materials, additives, preparation processes, and more and achieved significant results.<sup>84</sup> Specifically, Zhou et al.<sup>85</sup> compared and analyzed the performance of a polybenzimidazole membrane and Nafion membrane, and the results showed that VRFBs with a polybenzimidazole membrane had a higher CE and better capacity retention rate. Yu and Xi<sup>86</sup> have studied the problem of poor cycling stability of a sulfonated polyether ether ketone (SPEEK) membrane in VRFBs and adopted a hydrophilic porous polytetrafluoroethylene membrane as a sandwich structure for stress protection and an electrolyte buffer of the SPEEK membrane. The results indicated that the CE and EE of the battery were significantly improved. Ye et al.<sup>87</sup> prepared a hybrid membrane of superhydrophilic TiO<sub>2</sub> nanotubes dispersed in a Nafion matrix, which had high ion selectivity at 120 mA cm<sup>-2</sup>. Furthermore, the CE and EE of a VRFB with this membrane were 3.8% and 5.2% higher than those of the Nafion 212 membrane, respectively.

Then, Xu et al.<sup>88</sup> prepared a novel porous cross-linked polyimide membrane (PCrPI), which had ultrahigh chemical stability and could effectively block vanadium ion migration, reduce surface resistance, and had good durability. Moreover, the efficiency of the PCrPI membrane is significantly higher than Nafion 212. Khataee et al.<sup>89</sup> investigated the potential application of a 50  $\mu\text{m}$  thick anion exchange membrane based on poly(terphenyl piperidinium-*co*-trifluoroacetophenone) (PTPT) in a VRFB and found that the vanadium permeability of PTPT was significantly lower than that of the N212 membrane, with a primary capacity decay rate of 0.03%. Singh et al.<sup>90</sup> synthesized a cross-linked imidazole anion exchange membrane (AEM) by using an alkyl chain spacer, and the AEMs prepared by a cross-linked aliphatic polymer had good stable ionic conductivity and vanadium ion permeability resistance. Vanadium crossover has hindered the wide application of VRFBs, and Ghasemiestahbani et al.<sup>91</sup> developed a dual-function carrier molecular sieve membrane (CCMS), which effectively blocked the migration of hydrated vanadium ions. Although a variety of nonperfluorinated ion exchange membranes have been developed, their chemical stabilities are insufficient in the working environment of strong oxidation of VRFBs. On the basis of the above reasons, it is necessary to explore more novel ion-exchange membranes and find excellent ion exchange membranes that meet the working conditions of VRFBs.

Vanadium ion transport and cross-contamination have a significant impact on the performance of VRFBs. Developing high-performance membranes to break the balance between ion selectivity and conductivity is a huge challenge for VRFBs. To sum up, the application prospects of VRFBs are very broad. Therefore, it is of great significance to develop a new VRFB ion exchange membrane with high ionic conductivity, high ionic selectivity, strong chemical stability, low cost, and other factors to promote the industrialization of VRFBs. However, good stability and low preparation cost are often contradictory. If an ion membrane with excellent performance and low cost are prepared, it will be a breakthrough and become an important technical support for the energy storage industry.

**Bipolar Plate.** The BPP is an important part of the stack, which can collect the conduction current and separate the positive and negative electrodes–electrolytes. BPP should have the following characteristics: (i) can effectively separate the positive and negative electrolytes, (ii) has strong collection current capability, (iii) has strong antioxidant reduction, and (iv) supports the positive and negative electrodes. Therefore, the BPP should have high conductivity, good mechanical properties, good compactness, corrosion resistance, and high stability.<sup>92</sup> Similar to proton exchange membrane fuel cells, the BPP material which can be applied to VRFBs is mainly metal material, graphite material, and carbon–plastic composites.<sup>93</sup> Different materials manufactured by BPP in fuel cell applications are analyzed in the above reference. To illustrate these opinions in more detail, BPP materials are classified and summarized in Figure 9.

VRFB for large-scale energy storage requires consideration of material performance and cost. In all BPP materials, metal BPP corrosion resistance is the worst. Graphite BPP has strong corrosion resistance, but its toughness is poor and preparation process is complicated. Therefore, the need for ideal BPP materials is also an urgent task of VRFB research. In recent years, some scholars have focused on BPP research and achieved significant results. For example, Kim et al.<sup>95</sup> believed that the graphite BPP is relatively fragile, and the electrochemical

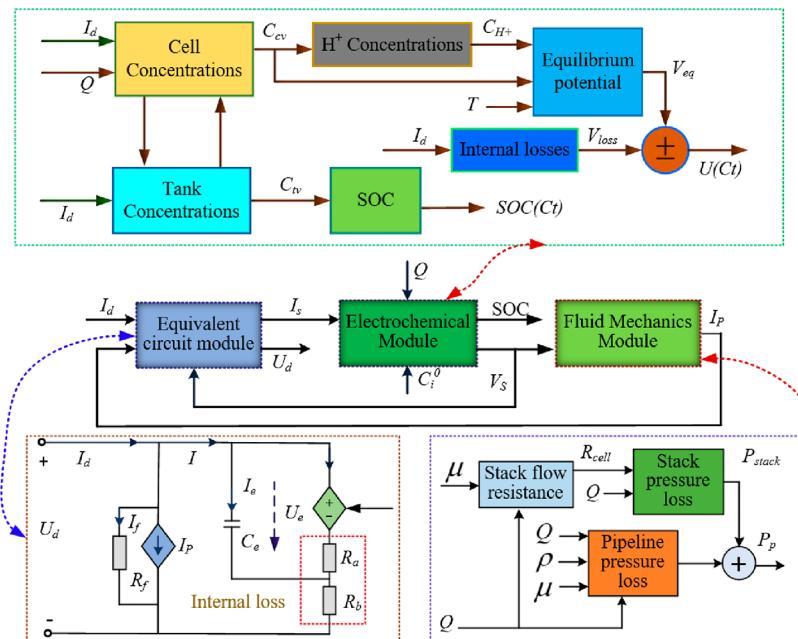


**Figure 9.** Classification of bipolar plate materials in VRFB applications. [Reproduced with permission from ref 94. Copyright 2021, Electrochemical Society.]

properties are unstable, increasing the cost of VRFBs. At the same time, a carbon composite BPP is proposed, and its EE and VE can be observed by recharge power experiments, and the durability of the composite BPP can be estimated. Choe et al.<sup>96</sup> designed a corrugated carbon/epoxy composite BPP for VRFBs to improve flow rate efficiency and reduce area-specific ratio resistance to further optimize the shape of the BPP to reduce ohmic polarization of the cell and pump power loss. Liao et al.<sup>97</sup> prepared a novel low-carbon-content BPP of a graphene carbon, fiber, and graphite powder mixed conductive material. The cell morphology, antibend strength, conductivity, corrosion resistance, vanadium permeability, and single battery performance have been studied and discussed. The results show that the BPP can reduce region-specific resistance and improve conductivity. Kim et al.<sup>98</sup> added polytetrafluoroethylene (PTFE) in the expanded graphite BPP, and the PTFE additive increased flexibility and enhanced the flexibility of the BPP. Therefore, the BPP has a low cost and the potential to rapidly and continuously prepare high-performance VRFBs. Satola<sup>94</sup> believed that if the BPP will be exposed to harsh conditions, the material needs to have good conductivity, sufficient impermeability and mechanical stability, and long-term chemical and electrochemical resistivities. So the preferred carbon–polymer matrix composite for a VRFB BPP was proposed.

The BPP is an important part of the VRFB combination, which should have good electrical conductivity, mechanical stability and impermeability, and other important characteristics and is used to connect and physically separate adjacent cells. BPP performance, the promotion of the preparation process, and the decline in cost can provide support for the development of large-scale VRFB electric stacks and modules.<sup>99</sup> Given these factors, in the process of design optimization and preparation of BPP, the best binding point should be found before the mechanical stability of conductivity and corrosion resistance.

The material is the material foundation for the preparation of VRFBs. The key material of the energy storage unit is the electrolyte. The key materials of the power unit are electrodes, membranes, and bipolar plates. However, the key technical indicators and reliability of the reactor are usually significantly lower than that of the single cell. Therefore, it cannot be solved by improving the performance of the cell material alone. In summary, the material challenges from monomer to reactor should be discussed from the following aspects: (i) Since manufacturing tolerances exist in the process of material processing and stack assembly, the internal resistance of the stack is inconsistent. Therefore, materials with minimum internal support deviation are developed during the production



**Figure 10.** Vanadium redox flow battery modular modeling. [Reproduced with permission from ref 164. Copyright 2021, Elsevier.]

of cells to reduce the inconsistency of internal resistance. (ii) The operating temperature range of a VRFB is narrow. The stack is composed of multiple monomers, and there is heat accumulation in the operation, which requires good heat transfer characteristics of materials and uniform temperature distribution. (iii) A stack is composed of a single series or parallel connection and through the fastening assemblage. The close degree between the critical components and electrode contact resistance caused by different active areas is different, which causes the component's mechanical failure and poor electrochemical performance. Therefore, the above factors should be fully considered when studying the critical component materials to improve the reliability of the stack.

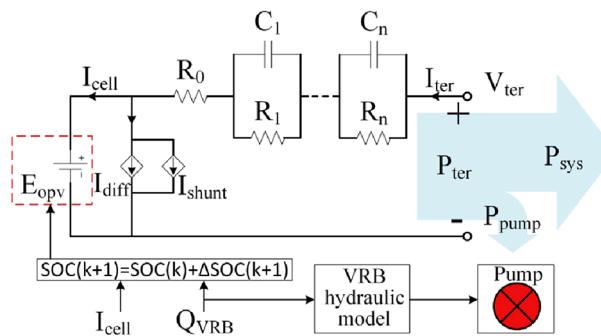
## VANADIUM REDOX FLOW BATTERY SYSTEM MODELING

To promote the practicality and commercialization of VRFBs, it is necessary to solve technical problems that affect the cost of the VRFB system and the reliability of operation. The current VRFB faces a series of problems such as uneven distribution of electrolytes, concentration polarization, vanadium deposition, heat accumulation, and low system reliability.<sup>100</sup> To solve the VRFB problems, an in-depth understanding is needed of the microscopic process of the battery, the performance parameters of the battery, membrane, and electrolyte, and the impacts of operating parameters on the internal parameters of the battery and on the performance of the battery need explored. However, it is more difficult and expensive to carry out experimental research, so some experiments cannot be done. Therefore, modeling analysis is very important. Recently, numerical modeling and simulation have been not only valid tools for the potential mechanisms of VRFBs at different space and time scales but have also optimized the VRFB according to the system model to obtain optimal battery performance.<sup>42</sup>

After reviewing the literature on VRFBs in recent years, research on VRFB models is analyzed and summarized. The VRFB model mainly includes an equivalent circuit model, electrochemical model, and hybrid model. But attention is

needed because those models have significant differences. To distinguish this knowledge, Figure 10 shows a process of realization of VRFB modeling involving physical, chemical, and electrical characteristics, mechanics, and temperature of the battery. To sum up, accurate modeling is an essential tool for battery design and optimization, saving time and reducing costs.

**Equivalent Circuit Model.** The equivalent circuit is the most common modeling method for the VRFB, and the idea comes from the traditional solid-state battery. The method starts from the perspective of physical mechanisms, using some ideal components such as resistance, capacitance, inductance, and a controlled source to simulate the physical phenomenon generated during the electrochemical process. Therefore, the modeling method is simple, easy to operate, easy to obtain parameters, and has strong applicability. For its applications in VRFBs, the equivalent circuit models include the Devonian equivalent circuit, RC equivalent circuit, thermal coupling model, and comprehensive equivalent circuit model.<sup>101–103</sup> Zhang et al.<sup>104</sup> believed that the electrical equivalent circuit model had good adaptability and simplicity in predicting the electrical dynamic response of the VRFB system, although few people have studied it. Therefore, a comprehensive electrical equivalent circuit model (Figure 11) of a VRFB has been established for system-level analysis. Experiments show that the model has excellent accuracy and can effectively determine the optimal flow rate under the maximum SE. Bhattacharjee et al.<sup>105</sup> established a precision dynamic equivalent circuit model and believed that the internal parameters of the battery are related to flow rate, stack current, SOC, and operational cycle number. The results showed that the average error of charging of the VRFB stack voltage is reduced by 28% and average error of discharge by 14% compared to the static model. This model can be used for dynamic parameters extraction and loss optimization. Conventional static equivalent circuit models are simple to model and can meet simple charge and discharge conditions, but it is difficult to meet the needs of external circuit characteristics. Therefore, there is less research on the equivalent circuit. To obtain high-precision battery performance



**Figure 11.** Comprehensive electrical equivalent circuit model for VRFBs. [Reproduced with permission from ref 104. Copyright 2015, Elsevier.]

parameters, it is used to correct and verify the static model, and the dynamic equivalent circuit model is required to be systematically established, which can improve the accuracy of the model and can also extend the precision of the VRFB model on this basis.

**Electrochemical Model.** The electrochemical model is based on the electrochemical process of the internal reaction of the battery, considering factors such as flow field, electric field, concentration field, temperature field, and electrochemical reaction in the battery operation.<sup>106</sup> Early research on electrochemical models mainly focused on the battery overall performance, lacking electrochemical characteristics of the battery itself. To further explore the electrochemical characteristics of the battery, the elevated electrochemical mathematical model needs to fully consider the relationship between the

parameters of the battery and set up a full battery value from the energy conservation angle, combined with energy Steve equations, Bernoulli equations, and related experience equations to establish a full battery value.

Through the Nernst equation, the electrolyte concentration was found to affect the balance potential of a VRFB. With vanadium and hydrogen ion concentrations in a given VRFB stack, the calculation of the balance potential  $E_{OCV}$  is eq 6.<sup>107</sup>

$$E_{OCV} = E^0 + \frac{RT}{zF} \ln \left( \frac{C_{V^{5+}}(C_H^+)^2 C_{V^{2+}}}{C_{V^{4+}} C_{V^{3+}}} \right) \quad (6)$$

The range of SOC is between 0 and 1, which is a measure of the remaining energy in the storage tank. Because  $C_{V^{2+}} = C_{V^{5+}}$  and  $C_{V^{3+}} = C_{V^{4+}}$ , then the values of the SOC in the positive and negative poles are consistent.<sup>108</sup> The expression of SOC is as follows

$$SOC = \frac{C_{V^{2+}}}{C_{V^{2+}} + C_{V^{3+}}} = \frac{C_{V^{5+}}}{C_{V^{4+}} + C_{V^{5+}}} \quad (7)$$

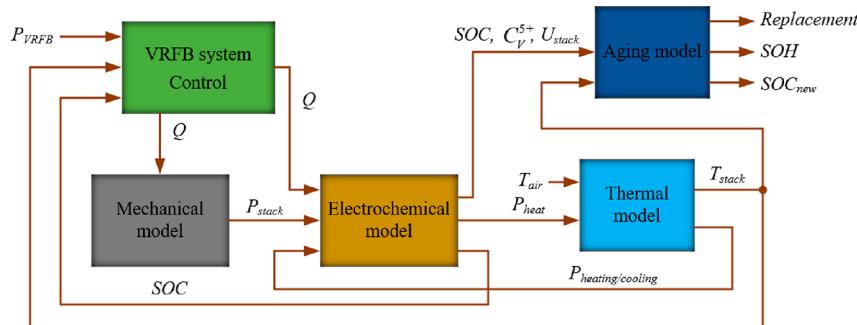
In the positive electrolytic solution,  $C_{V^{5+}} \propto SOC$  and  $C_{V^{4+}} \propto (1 - SOC)$ ; in the negative electrolyte,  $C_{V^{2+}} \propto SOC$  and  $C_{V^{3+}} \propto (1 - SOC)$ . It can be seen from the above formula that the balance potential of the battery is related to the SOC.<sup>109</sup>

$$E_{OCV} = E^0 + \frac{2RT}{zF} \ln H^+ + \frac{2RT}{zF} \ln \frac{SOC}{1 - SOC} \quad (8)$$

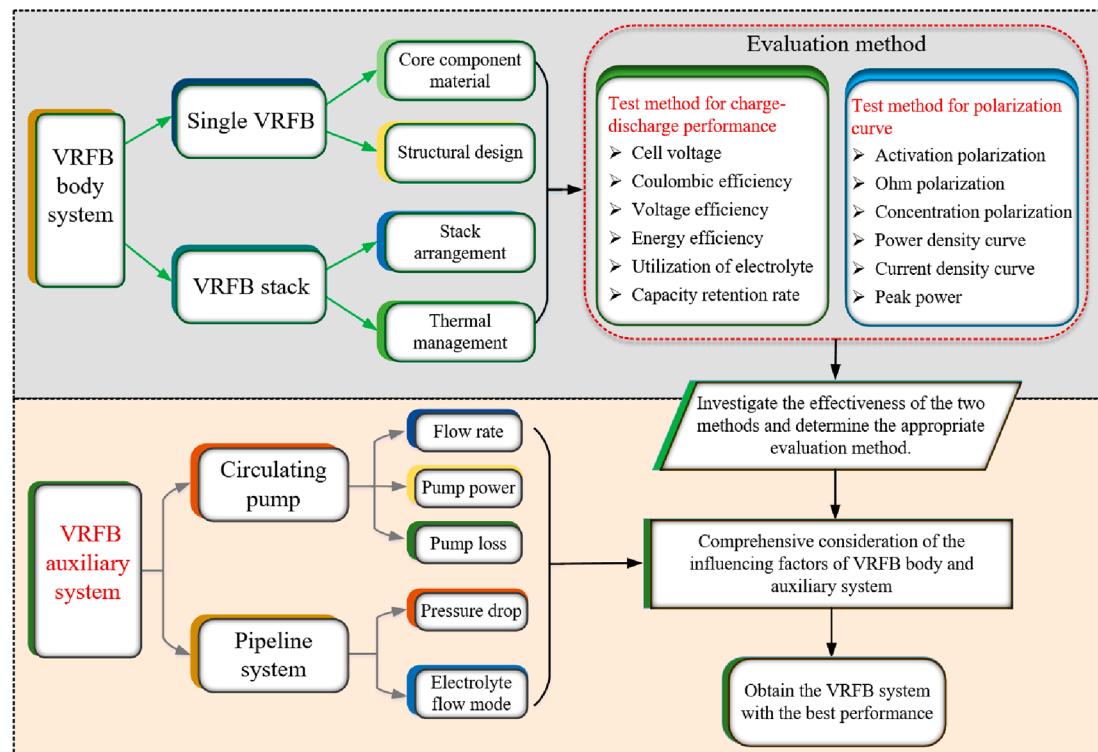
The VRFB electrochemical model can be used to understand the process of battery reactions, material and temperature changes, and more, which has certain theoretical guiding significance for the structural design, flow rate optimization,

**Table 1.** Charge, Mass, and Momentum Conservation Equation in VRFB

Name	Expression	Parameter definition
Charge conservation equation	$\sum_i Z_i C_i = 0$	<ul style="list-style-type: none"> <li>• <math>\epsilon</math> is the electrode porosity</li> <li>• <math>c_i</math> is the concentration of species</li> </ul>
Mass conservation equation	$\frac{\partial}{\partial t} (\epsilon c_i) + \nabla \cdot \vec{N}_i = -S_i$ $\vec{N}_i = -D_i^{eff} \nabla c_i - Z_i K_i F c_i \nabla \phi_i + \vec{u} c_i$ $D_i^{eff} = \epsilon^{1.5} D_i$ $\vec{u} = K / \mu \nabla p$ $K = \frac{d_f^2 \epsilon^3}{K_{CK}(1 - \epsilon)}$	<ul style="list-style-type: none"> <li>• <math>D_i</math> is the diffusion coefficient</li> <li>• <math>Z_i</math> is the valence of species</li> <li>• <math>K_i</math> is the ionic mobility of species</li> <li>• <math>\phi_i</math> is the ionic potential</li> <li>• <math>\vec{u}</math> is the electrolyte velocity</li> <li>• <math>F</math> is the Faraday constant</li> <li>• <math>K_{CK}</math> is the Kozeny-Carman constant</li> <li>• <math>d_f</math> is the fiber diameter</li> <li>• <math>S_i</math> is the source term</li> </ul>
Momentum conservation equation	$\nabla \cdot \vec{u} = 0$ $\rho(\nabla \cdot \vec{u}) = -\nabla p + u \nabla^2 \vec{u}$ $\vec{N}_{H^+} = -\frac{\sigma_{mem}}{F} \nabla \phi_{mem}$	<ul style="list-style-type: none"> <li>• <math>\rho</math> is the electrolyte density</li> <li>• <math>u</math> is the dynamic viscosity of the fluid</li> <li>• <math>k_{pos}^0</math> and <math>k_{neg}^0</math> are the reaction rate constants</li> <li>• <math>\alpha_{pos}</math> and <math>\alpha_{neg}</math> are charge transfer coefficients</li> <li>• <math>A_s</math> is the specific surface area of the electrode.</li> </ul>
Butler–Volmer equation	$i_{neg} = i_{0,neg} \left[ \left( \frac{C_{V^{3+}}}{C_{V^{3+}}^*} \right) \exp \left( -\frac{\alpha_{neg} F}{RT} \eta_{neg} \right) - \left( \frac{C_{V^{2+}}}{C_{V^{2+}}^*} \right) \exp \left( \frac{(1 - \alpha_{neg}) F}{RT} \eta_{neg} \right) \right]$ $i_{pos} = i_{0,pos} \left[ \left( \frac{C_{V^{5+}}}{C_{V^{5+}}^*} \right) \exp \left( -\frac{\alpha_{pos} F}{RT} \eta_{pos} \right) - \left( \frac{C_{V^{4+}}}{C_{V^{4+}}^*} \right) \exp \left( \frac{(1 - \alpha_{pos}) F}{RT} \eta_{pos} \right) \right]$	<ul style="list-style-type: none"> <li>• <math>\sigma_{mem}</math> is the conductivity of the membrane</li> <li>• <math>\phi_{mem}</math> is the electric potential of the membrane</li> <li>• <math>p</math> is the pressure</li> </ul>
Exchange current density	$i_{0,pos} = A_s F k_{pos}^0 C_{V^{5+}}^{*\alpha_{pos}} (1 - \alpha_{pos}) C_{V^{4+}}^{*\alpha_{pos}}$ $i_{0,neg} = A_s F k_{neg}^0 C_{V^{3+}}^{*\alpha_{neg}} (1 - \alpha_{neg}) C_{V^{2+}}^{*\alpha_{neg}}$	



**Figure 12.** Multiphysics models for VRFBs. [Reproduced with permission from ref 106. Copyright 2020, American Chemical Society.]



**Figure 13.** Modular methods for obtaining optimal VRFB performance parameters.

electrode design, and membrane research on improved and optimized battery bodies.

**Multiphysics Coupling Model.** The existing equivalent circuit model is often due to a lack of coupling with fluid mechanics models, and the influence of flow on the performances and efficiencies of VRFBs is unsatisfactory. Therefore, it is not perfect in actual project applications.<sup>110</sup> In addition, the simple fluid mechanics model is too simplified for the electrical characteristics of the battery itself, and the characteristics of the full vanadium flow battery system cannot be fully reflected. In comparison, the hybrid model shows a distinct advantage, and it can be used to describe the working process of a VRFB after integrating two or more modeling methods into a certain method.<sup>111</sup> The mixed model starts from the VRFB operating mechanism, overcoming the problem of a single modeling method itself, and can effectively reflect the battery's charge and discharge dynamic characteristics and the external equivalent characteristics. The charge, mass, and momentum conservation equations of the VRFB are shown in Table 1.<sup>112–114</sup>

In recent years, a large number of multiphysical coupling models have been studied. Sauer et al.<sup>115</sup> proposed a VRFB

multiphysical field coupling model considering electrochemical reactions, pump loss, VRB internal temperature changes, and aging predicted. This model is suitable for VRFBs of different grades of capacities and powers (Figure 12). Messaggi et al.<sup>116</sup> established a VRFB fluid mechanics and electrochemical coupling model for the simulation of interdigitated and serpentine fields of 25 cm<sup>2</sup>. The result showed that the serpentine flow field performance is good, but the auxiliary system loss is high. The interdigitated field reduced the unevenness and pressure drop of the electrolyte. Merei et al.<sup>117</sup> established a multiphysics model of VRFBs for aging forecasts for VRFBs. This model considers factors such as mechanical loss, temperature changes, and battery side reactions, and determines the key parameters of the aging of the battery. Castro et al.<sup>118</sup> studied VRFBs to improve multibattery design, electrochemical measurement, and thermal performance distribution, but through traditional experiments, this could not be realized. Therefore, this is achieved by developing multiphysical models. With increasing studies on the VRFB model, the focus of future research is to consider the

**Table 2.** Main Attributes and Performance Metrics of VRFBs

Name	Remarks	Expression
Energy density	Ratio of discharge energy and overcharge energy at a certain current density	$\text{Energy density} = \frac{nCFV_{dis}}{N_{\text{tank}}}$
Power density	Ratio of average voltage during discharge to average voltage during charging	Power density = Current density $\times \bar{V}_{dis}$
Current density	Current applied per membrane area	$i = nFv = nFD\left(\frac{C_{\text{bulk}} - C_{\text{surface}}}{\delta}\right)$
Ohmic polarization ( $\eta_{ohm}$ )	Used to overcome the internal resistance of the battery assembly associated with BPP, electrode, electrolyte, and membrane	$\eta_{ohm} = IR_{ohm} = \frac{Iw}{\sigma}$
Activation polarization ( $\eta_{act}$ )	Activation overpotential is potential difference required to overcome activation energy of cell reaction to produce current	$\eta_{act} = i_{0,\text{electrode}} \left[ \exp\left(\frac{\alpha_a F}{RT}\eta_{act,\text{electrode}}\right) - \exp\left(-\frac{\alpha_c F}{RT}\eta_{act,\text{electrode}}\right) \right]$
Concentration polarization ( $\eta_{con}$ )	Concentration overpotential is caused by gradient of concentration of reacting substances on electrode surface and in bulk electrolyte	$\eta_{con} = \frac{RT}{zF} \ln\left(1 - \frac{i}{i_{Lim}}\right)$ , $i_{Lim} = zFk_m C_r$
Capacity decay rate	Capacity decay in percentage over a total test duration time (% per day) or cycle number (% per cycle); total duration or cycle number should be reported along with decay rate	Slope of capacity time or capacity cycle number plots divide by initial capacity (% per day or % per cycle)
Theoretical capacity	Theoretical capacity of electrochemical cell is defined as number of electric charge present in cell	$Q_t = \frac{ncvF}{3600} = xnF$
State of charge (SOC)	Charged capacity stored over theoretical capacity denotes amount of battery capacity which can be utilized	$\text{SOC} = \frac{Q_{\text{char}}}{Q_t} = \frac{C_{V^{2+}}}{C_{V^{2+}} + C_{V^{3+}}} = \frac{C_{V^{5+}}}{C_{V^{4+}} + C_{V^{5+}}}$
Pressure losses ( $p_{loss}$ )	Pressure loss is derived from pipeline, electrode, and flow field frame; it is pressure difference between electrolyte in inlet and outlet	$p_{loss} = P_{\text{major}} + P_{\text{minor}} + P_{\text{felt}} = \lambda \frac{L}{d} \left(\frac{\rho v^2}{2}\right) + f_L \left(\frac{\rho v^2}{2}\right) + \mu \frac{L_e Q}{kA}$
Pump loss ( $P_{pump}$ )	Pump loss is used to measure indicators of pump configuration and operating conditions	$P_{pump} = \frac{p_{loss} Q}{\psi}$
Area-specific resistance (ASR)	Average specific resistance during galvanostatic charging and discharging can be calculated approximately	$\rho = \frac{V_0}{j} \left( \frac{1 - VE}{1 + VE} \right)$

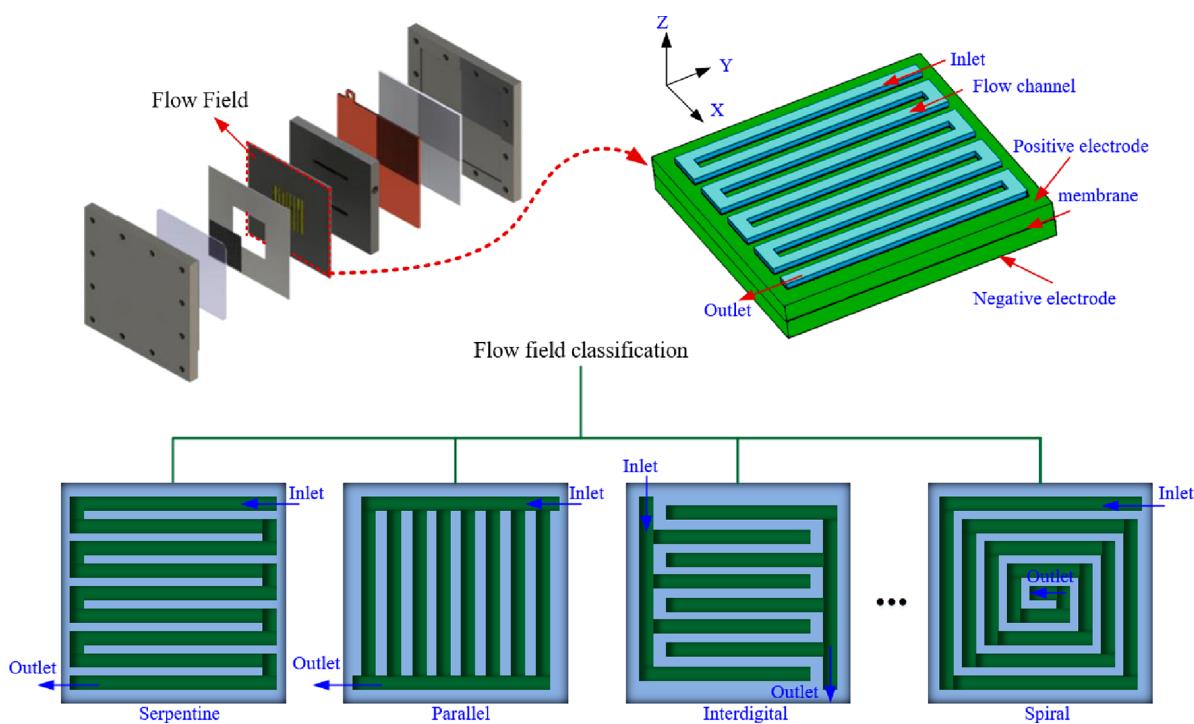
establishment of various factors to for multiphysics coupling models.

**Development and Prospects of Other Models of VRFBs.** Currently, models for VRFBs are mainly concentrated in equivalent circuit models, electrochemical models, and multiphysical field coupling models. In order to obtain more battery operation information and parameters, the model is critical. Xu and Zhao<sup>119</sup> summarizes the latest RFB research progress and introduces the future and potential of the modeling method such as the porous medium model, the lattice Boltzmann method, and the stack-level network model. Chou et al.<sup>50</sup> discuss that VRFB modeling is of great significance to the improvement of the battery. The modeling method is roughly divided into three categories: macro method, micro method, and molecular/atomic method. The method, application, effectiveness, and limitations of VRFB modelings are discussed. The macro method comprises the empirical model, Monte Carlo model, equivalent circuit model, lumped parameter model, and continuum model. The micro method is related to the Lattice Boltzmann method. The molecular/atomic method is based on the modeling of density functional theory and molecular dynamics. Accurate modeling can effectively guide the battery structure design and optimization operation and accelerate research and development speed. Therefore, considering the internal and external characteristics of the battery, combined with liquid phase mass transfer, heat transfer, and electrochemical reactions, it is possible to find and develop models suitable for VRFBs, thereby achieving optimization and innovation of battery structures.

## OPERATIONAL OPTIMIZATION

Because of the uniqueness of the materials and structural functions of the internal components of batteries, operational optimization is another key to improving the performance of VRFBs. After reviewing the existing literature, a clear conclusion can be drawn that the structure design and optimization mainly are focused on the design and optimization of the flow channel, the structure design of the BPP, the structure optimization of the membrane, and the structure optimization of the stack. Figure 13 shows designs and optimizations VRFBs. Moreover, the research level of VRFBs can be divided into single cell and stack. On the one hand, the single cell is mainly for the core material research and development of batteries and the design and optimization of flow field structure. On the other hand, stack optimization is mainly used to explore the topology and heat transfer behavior of batteries. In many cases, a unified approach needs to be followed that designs a single cell or stack first, applies battery performance evaluation methods, then optimizes the battery parameters, which results in an optimal battery structure. However, a complete VRFB system must include electrolysis, electrolyte transmission equipment, and PCS. Therefore, it is necessary to fully consider the pump power, pump loss, and pressure drop such as the VRFB assist system, and reduce the energy loss of the auxiliary system. The operation optimization performance of the battery will be evaluated through the main battery attributes and performance metrics in Table 2. At the same time, combined with electrolysis and the auxiliary system, the VRFB system can obtain an optimal SE.<sup>120</sup>

In the operation process of a VRFB, there are some phenomena such as uneven electrolyte distribution, flow dead



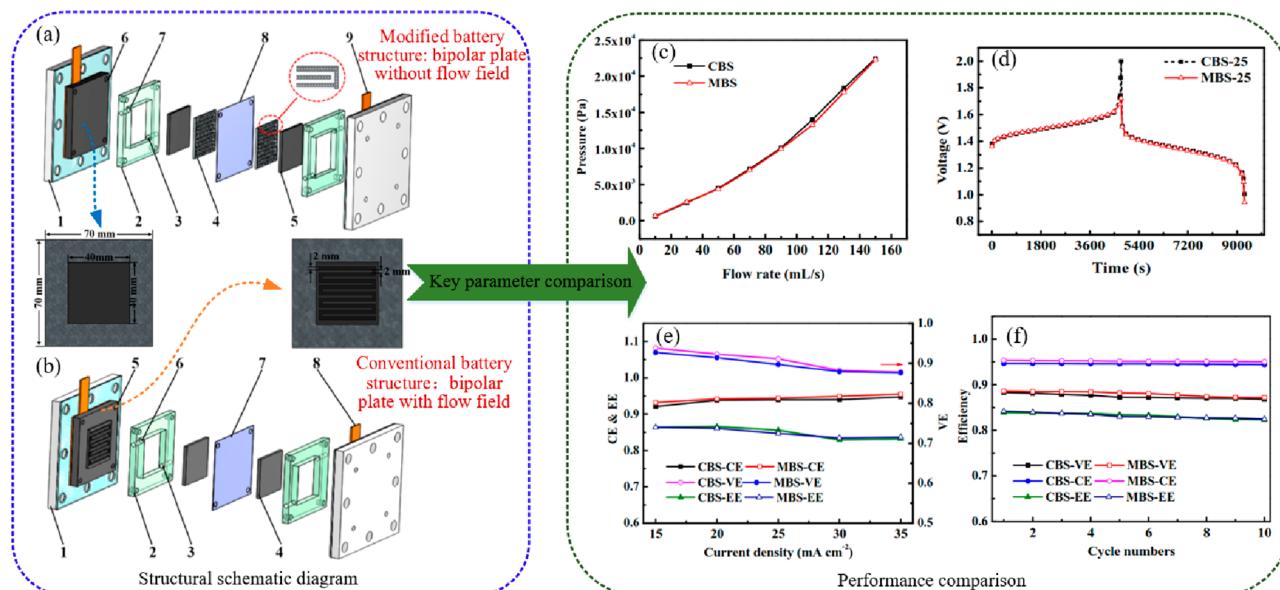
**Figure 14.** VRFB flow field classification.

zone, vanadium ion diffusion, hydrogen and oxygen evolution side reactions, electrolyte imbalance, capacity attenuation, self-discharge, mass transfer obstruction, and local polarization, which lead to the decrease of battery efficiency and affect the overall performance of the battery.<sup>121</sup> Fortunately, the above problems can be solved by operation optimization strategies such as flow field design, flow rate optimization, stack optimization, and reduced energy consumption, so that the VRFB system is operating at the optimal state. Therefore, extensive commercialization of VRFBs can be achieved by optimizing battery operation to improve overall battery performance and reduce the cost of key components. In this context, the structural design and operation optimization of the VRFB system is a convenient method to improve the performance of the battery, usually without a huge improvement cost, and the optimization of operating parameters is of great significance in the industrial applications of battery systems.

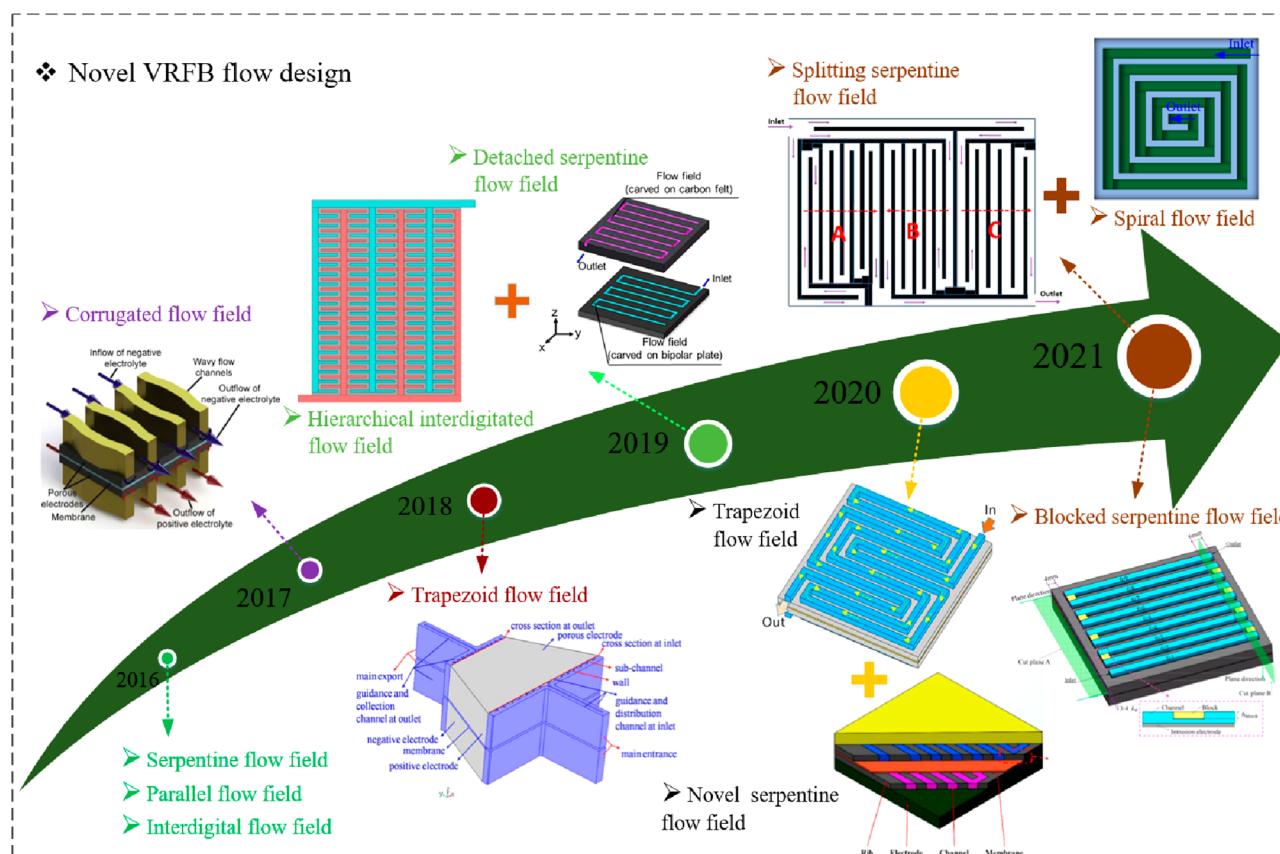
**Flow Field Design and Flow Rate Optimization.** The flow field is an important place to provide electrochemical reactions in VRFBs which directly affect the flow characteristics of the electrolyte, which in turn affect the liquid phase mass transfer process of the electrode surface and ultimately affect the performance of the battery. Flow field design and flow rate optimization are effective ways to improve battery performance without a huge improvement cost.<sup>122</sup> At this stage of the studies, researchers are dedicated to the design and optimization of high-performance flow fields to ensure that the electrolyte flows evenly and well within the battery, resulting in the efficient and stable operation of VRFBs.

The research idea of the VRFB internal flow field design comes from the flow field structure of the fuel cell. The flow collecting plate of a VRFB is engraved with inlet and outlet electrolyte diversion channels. Figure 14 classifies the VRFB flow field studied in the existing literature, including serpentine flow field, parallel flow field, interdigital flow field, and spiral flow field. Xu et al.<sup>123</sup> designed and compared the influence of with

and without a flow channel-flow field, serpentine flow field, and parallel flow field on battery performance. Studies have shown that serpentine flow fields can improve the distribution uniformity of electrolytes, alleviate the polarization of concentration, and improve the overall performance of the battery. Ali et al.<sup>124</sup> minimized the flow dead zone of the electrolyte inside the electrode and designed and compared a multichannel (1–4 channel) serpentine flow field on the collector plate. Numerical simulation results show that a reasonable number of channels can obtain the best battery pressure drop and performance. García-Salaberri et al.<sup>125</sup> believe that flow fields can improve battery performance and efficiency while reducing costs. The interdigital flow field refers to a conical cross section designed and compared with a constant cross section of the interdigital flow field in terms of flow distribution and pressure drop characteristics. The results show that the cone section changes the flow rate of the inlet and outlet of the electrolyte, alleviates the local concentration polarization, and increases the battery efficiency but increases the pressure drop inside the battery. Lee et al.<sup>112</sup> explored the effects of five flow channel sizes and the flow rate on battery power based on serpentine. Studies have shown that reducing the flow channel size and increasing the flow rate can improve the electrochemical performance of the battery but increase the pressure drop between the inlet and outlet. Li et al.<sup>126</sup> believe that the spacing between adjacent interdigitated channels is the key parameter of VRFB interdigitated flow field design, which directly affects the distribution and size of electrolyte flow, resulting in pump loss and mass transfer loss. Numerical analysis shows that the optimal flow channel spacing at different current densities and flow rate is 3 mm. Gundlapalli and Jayanti<sup>127</sup> did eight variations of channel and rib dimensions in the area of 400 cm<sup>2</sup> and 900 cm<sup>2</sup> based on the serpentine flow field. The results show that in a larger battery there is a significant improvement in the sensitivity of the channel size, the pressure drop, peak power density, and discharge energy density. It is recommended to increase the



**Figure 15.** Vanadium redox flow battery bipolar plate structure modification: (a) modified battery structure, (b) conventional battery structure, (c) pressure drops of CBS and MBS under various flow rates, (d) galvanostatic charging–discharging profiles of CBS and MBS at current density of  $25 \text{ mA cm}^{-2}$ , (e) efficiencies under various current densities, and (f) efficiencies of 10 cycles under current density of  $25 \text{ mA cm}^{-2}$ . [Reproduced with permission from reference 128. Copyright 2019, Elsevier.]



**Figure 16.** Other novel flow field designs for VRFBs.

width of the flow channel and reduce the rib width to effectively improve the overall performance of the battery. Duan et al.<sup>128</sup> believes that the BPP design of the conventional battery structure (CBS) with a flow channel introduces more severe oxidation corrosion. Therefore, a modified battery structure

(MBS) is proposed to separate the BPP and flow channel design. The results show that an improved structure of the battery can maintain flow characteristics and energy efficiency and has higher CE (Figure 15).

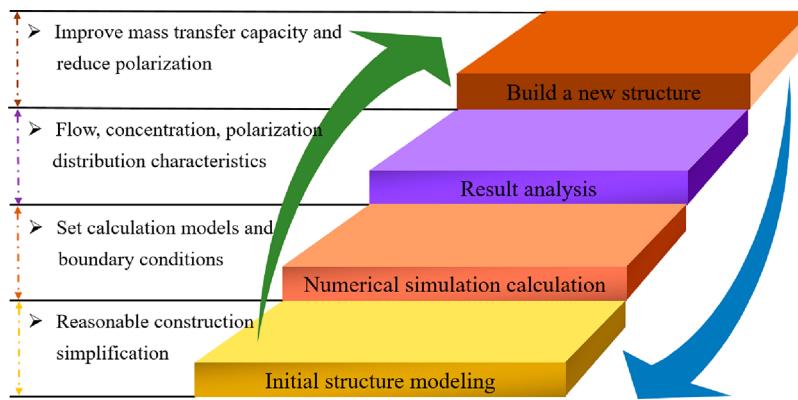
**Table 3.** Analysis of Some Important Literature on Novel Flow Field Design of Vanadium Redox Flow Battery

Flow field name	ref	Author	Year	Flow field description	Research purposes
Corrugated flow field	134	Lisboa et al.	2017	• Novel mass transfer enhancement concept for RFB proposed, which improved rectangular flow channel into trapezoidal wave type	◆ Improve transmission characteristics ◆ Increase power density ◆ Improve battery performance
Multidistribution channels flow field	135	Wu et al.	2017	• Single inlet and outlet flow field frames improved to multichannel flow field	◆ Improve electrolyte distribution ◆ Improve energy efficiency
Trapezoid flow field	136	Yue et al.	2018	• New trapezoidal RFB proposed for first time due to uneven distribution of concentration and polarization in conventional rectangular flow cell	◆ Enhance the mass transport ◆ Improve VE ◆ Improve electrolyte utilization
Hierarchical interdigitated flow field	137	Zeng et al.	2019	• Hierarchical set of flow field proposed, which independently adjusted allocation/collection channels	◆ Enhance mass transport ◆ Lower pumping loss ◆ Low-pressure drop
Detached serpentine flow field	138	Sun et al.	2019	• Flow field applies two interlaced serpentines to BPP and electrodes	◆ Enhance mass transfer capacity ◆ Reduce pressure drop
Rotary serpentine flow field	139	Lu et al.	2020	• Traditional serpentine flow field improved into rotating serpentine flow field to increase electrolyte flow and distribution	◆ Increase electrolyte permeability ◆ Improved species distribution ◆ Improve net discharge power
Novel serpentine flow field	140	Sun et al.	2020	• Adjust position of flow channel and electrode, increase effective area of membrane, reduce resistance, and improve voltage efficiency (VE)	◆ Decrease contact resistance ◆ Improve VE
Splitting serpentine flow field	141	Gundlapalli and Jayanti	2021	• Divide flow field into plurality of parts to quickly empty reaction product	◆ Reduce ion resistance ◆ Improve electrochemical performance ◆ Reduce pressure drop
Blocked serpentine flow field	142	Yang et al.	2021	• Increase height of 1.4 mm in corner of serpentine, improve penetration and convection of electrolyte in porous electrode	◆ Improvement of penetration and convection ◆ Improve SE ◆ Reduce pump loss
Spiral serpentine flow field	143	Huang et al.	2021	• Flow channel changed to spiral shape based on serpentine flow field, flow characteristics of electrolyte used	◆ Improve SE ◆ Improve the uniformity of electrolyte flow ◆ Mitigation concentration polarization

The purpose of VRFB flow field design is as follows: (1) improve battery electrolyte uniformity, reduce local flow dead zones and concentration polarization, and improve battery efficiency and operating stability<sup>129</sup> and (2) reduce mass transfer resistance, improve electrolyte flow, and reduce ohmic polarization and concentration, thereby increasing the overall performance of the battery.<sup>130</sup> Structure optimization of traditional flow fields should consider attributes and performance metrics such as battery voltage, polarization, current density, capacity attenuation rate, SOC, battery efficiency, power density, ion intersection, and electrolyte imbalance. Obtaining the best flow field geometry and configuration through performance testing fundamentally improves the overall performance of the battery.

The flow field design is a more convenient way to improve battery performance, usually with no more cost. Excellent flow fields can effectively improve the distribution of electrolyte distribution and reduce the transmission resistance of electrolytes. Therefore, in VRFB research, researchers are committed to

the exploration and development of novel flow fields. Figure 16 shows some important novel flow field designs of VRFBs in the recent five years to emphasize the importance of flow field design and describe the trend of flow field design. At present, the research on VRFB flow field design is mainly concentrated on a monomer battery, which is limited to traditional square batteries and cross-sectional designs. Therefore, battery performance is not significant and lacks exploration of innovative battery structure. The method should be used to guide the optimal design of the battery flow field structure in numerical modeling and simulation methods. The scientific and reasonable flow field structure ensures a uniform flow of electrolytes in the battery and is a prerequisite for achieving efficient and stable operation of the battery. Novel flow field design and flow optimization are effective ways to improve battery performance, which has the characteristics of a short design cycle, low cost, and high safety. Table 3 is the key analysis of some novel flow field design literature. The flow rate, assembly parameters, and other factors affect the internal running process of the battery, and the



**Figure 17.** Design and optimization ideas of a VRFB stack structure.

**Table 4. Vanadium Redox Flow Battery Efficiency Evaluation System**

Efficiency name	Definition	Expression
Coulomb efficiency (CE)	Ratio of discharge capacity to charge capacity	$CE = \frac{\int I_{dis}(t)dt}{\int I_{ch}(t)dt} \times 100\%$
Voltage efficiency (VE)	Ratio of average voltage during discharge to average voltage during charging	$VE = \frac{\int V_{dis}(t)dt / \int V_{ch}(t)dt}{t_{dis}/t_{ch}} \times 100\%$
Energy efficiency (EE)	Ratio of discharge energy to charging energy	$EE = \frac{\int V_{dis}(t)I_{dis}(t)dt}{\int V_{ch}(t)I_{ch}(t)dt} \times 100\%$
Utilization of electrolyte (UE)	Ratio of energy storage capacity to theoretical capacity	$UE = \frac{Q_{prac}}{Q_t} \times 100\%$
System efficiency (SE)	Ratio of system discharge output power to charging power consumption	$SE = \frac{\int_0^{t_{dis}} (P_{dis} - P_{loss})dt}{\int_0^{t_{ch}} (P_{ch} + P_{loss})dt} \times 100\%$

adaptation relationship with them should be considered when optimizing the flow field structure to realize the collaborative optimization of multiple factors.

**Stack Design and Optimization.** The structural design of a VRFB is limited to a single cell and lacks high-power stack applications. However, battery performance is not only related to the flow of electrolytes but also is associated with mass transfer, heat transfer, and more, and the entire electrochemical reaction process is quite complicated.<sup>131</sup> Therefore, it is necessary to establish a structural design and optimization of the stack level and implement the strategy of a VRFB numerical simulation guidance structure design in the structural design of stacks with high performance. The initial stack research was to increase the electrode surface area and the number of single cells to improve the power of the battery and now through the stack structure design optimization to improve the performance of the stack.<sup>132</sup>

The stack is the place of energy conversion in the VRFB system, and the performance of the stack is the basis of building a high-performance energy storage module. Figure 17 is the process of designing the VRFB stack design. During the design of the stack, the electrolysis structure is reasonably simplified, the model reasonably assumed, and the initial structural model established. On this basis, the appropriate control equation and boundary conditions for numerical simulation calculations are selected. The numerical simulation results of the electrolyte flow rate, reactant concentration, temperature, concentration polarization, and distribution characteristics in the stack were analyzed, and their relationship with the stack structure was

obtained. On this basis, the design idea of the stack structure to strengthen the liquid mass transfer in the stack and reduce the concentration polarization is put forward.<sup>133</sup> The performance of the newly designed stack is tested using a charging and discharging test and polarization curve test to judge whether its performance meets the design requirements. If the design requirements cannot be met, relevant parameters should be optimized until the requirements are met according to the feedback information.<sup>144</sup>

Reed et al.<sup>145</sup> developed a kW class VRFB stack and showed that polarization, flow rate, temperature, and electrode structure are key factors for stack performance. By improving the electrode microstructure and flow field design, the stack EE is nearly 75% at 320 mA/cm<sup>2</sup> and 50°C, and an improved stack EE can be translated into the whole SE being explored. Zhao et al.<sup>146</sup> studied the characteristics and performance of a 10 kW stack consisting of 14 batteries, with an EE of more than 80%, indicating that the VRFB is a promising and efficient energy storage technology. Chen et al.<sup>147</sup> found the phenomenon of transmission delay in multistack RFBs. Transmission delay will lead to uneven concentration distribution along the pipeline, resulting in poor uniformity of stack pressure in the module, which will lead to a premature pressure cutoff during operation and reduce capacity utilization. Therefore, based on optimizing the structure of the stack with a high variable flow rate and small pipe radius, the transport delay and its negative impact on the module can be effectively reduced by optimizing the electrolyte feeding mode. Zou et al.<sup>148</sup> built a 35 kW vanadium VRFB energy storage system. The flow rate of the system is adjusted by

changing the frequency of the AC pump and analyzing the energy efficiency, resistance, capacity loss, and energy loss of the stack system under each flow. The results showed that as the flow rate increases, the EE of the stack is improved. Also, the resistance of the electric stack is reduced, but the pump consumption increases significantly.

**Efficiency Analysis.** An accurate analysis of VRFB performance is the most intuitive and effective method to evaluate battery efficiency. The charge–discharge performance parameters mainly include CE, VE, EE, UE, and SE<sup>149</sup> Table 4 is the efficiency definition used to evaluate VRFB performance. CE is used to measure the energy conversion efficiency of a battery during charging and discharging. CE is mainly affected by a vanadium ion crossover self-discharge reaction, electrolyte leakage resulting in electrolyte loss, hydrogen evolution, and other irreversible side reactions, resulting in lower efficiency. VE is closely related to the polarization of batteries. The higher the VE is, the weaker the polarization, the smaller the voltage loss, the closer the charge and discharge voltage, and the closer the balance voltage. It is usually affected by the active polarization of the electrode, ohmic polarization of resistance between the electrolyte and ion conduction membrane, and concentration polarization of liquid mass transfer. In large-scale energy storage, EE is a key metric for measuring the availability of energy storage technology. Evaluation metrics are used to evaluate the energy conversion efficiency during charge and discharge. The UE is used to measure the amount of active substance involved in the electrochemical reaction in the electrolyte, associated with vanadium ion intersecting self-discharge and battery polarization.<sup>150</sup> In the VRFB system, the system power consists of the stack power and the auxiliary system power. The SE is equal to the ratio of the energy output of the VRFB energy storage system during discharge to the energy consumed during charging. SE is used to evaluate the performance of the entire VRFB system and to consider the overall performance of the stack and the battery assistance system.

**Capacity Attenuation Analysis.** The capacity of a VRFB is mainly determined by the volume and solubility of the electrolyte. Many factors cause VRFB capacity attenuation, including electrolyte leakage, electrolyte imbalance, self-discharge, vanadium crystallization, vanadium ion cross, water penetration, and more.<sup>151</sup> The diffusions of vanadium ions and side reactions have a significant effect on the capacity of a VRFB during the long cycle of charge and discharge. The differential diffusion rates of vanadium ions diffusing from one half cell to the other will promote a self-discharge reaction, resulting in an imbalance between the charged state of the electrolytes of the two half cells and the subsequent capacity attenuation.<sup>152</sup> The VFB capacity is further affected by side reactions resulting from hydrogen release or oxidation of  $V^{2+}$ . When electrolyte remixing or rebalancing should be done periodically to restore battery capacity is also an area of interest in VRFB research.<sup>153,154</sup> The decrease of VRFB capacity is related to the imbalance of the vanadium active substance and the asymmetry of the vanadium ion valence state. The asymmetrical valence state of vanadium ions results in a decrease of the SOC range of positive electrolytes and an increase of the SOC range of negative electrolytes. The polarization phenomenon is serious, and the capacity attenuation is aggravated.<sup>155</sup> More serious is the vanadium ion cross-reaction and the self-discharge reaction; this combined reaction further aggravates the capacity attenuation. Water penetration causes the an imbalance of positive and negative vanadium ion concentrations, leading to advanced

cutoff of the charge–discharge reaction; especially at low current density, electrolyte imbalance is more serious.<sup>156</sup>

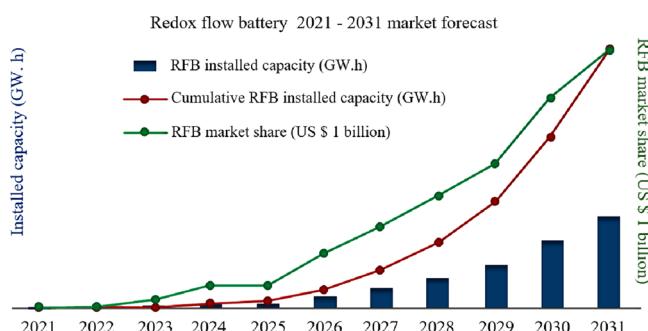
Capacity is a fundamental attribute of VRFBs, which determines how VRFBs can be utilized to work efficiently and keep the system running safely for optimal system cost. Therefore, it is necessary to grasp the mechanism and discipline of capacity attenuation and look for scientific and reasonable methods of capacity preservation and regeneration.<sup>157</sup> In recent years, how to improve capacity attenuation to reduce capacity attenuation has become a non-negligible direction. For example, Liu et al.<sup>158</sup> achieved higher electrolyte utilization by reducing the vanadium/proton ratio during long battery operation, thus increasing battery capacity. Luo et al.<sup>159</sup> proposed the current change strategy, which dynamically changed the impressed current density according to the real-time charging and discharging state, effectively reducing the concentration polarization and ohmic polarization and increasing the effective capacity by more than 10%. Park et al.<sup>160</sup> found that the cross imbalance of vanadium ions led to the rapid decay of the battery's early capacity and proposed that the asymmetric positive and negative electrolyte volume ratio could reduce the early capacity decay rate. Asymmetries between charge and discharge operations lead to water crossing and electrolyte imbalance, so Shin et al.<sup>161</sup> proposed that adding sulfuric acid with different concentrations in the electrolyte can reduce electrolyte imbalance. Considering that electrolyte imbalance leads to battery capacity attenuation, Jienkulsawad et al.<sup>162</sup> developed an online optimal operation strategy to obtain optimal vanadium flow and mitigate the capacity decline. It is very important to explore more capacity attenuation control methods and minimize capacity loss for VRFBs.

## BUSINESS CHALLENGE AND PERSPECTIVE

Large-scale stationary energy storage is mainly based on Li-ion energy storage. However, Li-ions are mainly used for terminal mobile energy storage, and lithium resources are becoming scarce. VRFBs will become the best ECS technology for stationary energy storage in the future. At present, VRFBs are affected by the system cost and encounter bottlenecks in promotion applications. Therefore, VRFBs are full of opportunities and challenges in large-scale commercial applications.

**Material Costs.** The main cost of the VRFB is concentrated in the stack (BPP, ion membrane, and electrode) and the electrolyte, and the cost of the two is about 85% of the total cost of the system. How to reduce the cost of the two is also a focus direction of VRFB research. Developing low-cost, high-performance component materials is the key to solving the cost of the stack. Attention should be paid to the following problems: (i) Cost reduction should not be at the cost of greatly sacrificing performance. (ii) The development of low cost and high-performance a BPP and ion membrane is an important way to reduce the cost of the stack. (iii) In addition to material cost and performance, focus should be placed on production cost and production efficiency.<sup>163</sup>

**Market Incentive Mechanism.** At present, the VRFB is low in electrochemical reservoirs, and the proportion is less than 1%. Because the VRFB is suitable for the energy storage area, with the large development of future energy storage, the VRFB is expected to rise rapidly. Many scholars predicted that the next 10 years of RFB technology will begin to occupy the Li-ion battery market and exceed the Li-ion battery capacity in 2031. RFB can store renewable energy such as sunshine, wind, or tide, and release it at needed.<sup>164</sup> Figure 18 shows the market



**Figure 18.** RFB future market forecast (Image Source: IDTECHEX: Vanadium battery challenges lithium battery market).

prospects for flow batteries. In the next decade, there will be significant growth in the installed capacity, growth rate, market share, and other aspects. The flow battery market is expected to reach billions of dollars by 2031. To face energy crises, more and more countries have implemented green economic policies, energy scenarios are changing, and the role of energy storage in the grid is accommodated in variable renewable energy. The intermittent problem of wind and photovoltaic will be resolved, and RFB will usher in high-speed development in the next decade and will bring a great impact on the Li-ion battery market.<sup>165</sup>

Although VRFBs have significant advantages in large-scale energy storage applications, the lack of market incentive mechanisms leads to the advantage of market share. Therefore, it is important to develop strong incentive mechanisms to industrialize and commercialize fully. VRFB energy storage should follow the following basic principles in the existing market mechanism: (i) Market access conditions and the main positioning of the VRFB application are clarified. (ii) Design of the market mechanism should be carried out step by step according to local conditions. (iii) Participating in the market mechanism should follow the rules and should conduct overall market design and resource planning, continuously adjusting as needed.

**Development Trend of VRFB.** VRFBs have some disadvantages including large volume and being not easy to handle, but the advantages are also very prominent as follows: They have long service lives of up to 20 years. Electrolytes can be recycled. Battery capacity is expandable, which can be used to build kW to 100 MW energy storage power stations. They do not burn easily. They have good safety. They can achieve 100% discharge without damaging the battery. In summary, VRFBs are very suitable for energy storage batteries, especially in photovoltaic, wind, and power fields and other new energy fields.<sup>166</sup> Table 5 shows a comparison of the main ECS batteries that can be largely integrated. Analysis shows that VRFBs have significant advantages, while the most prominent disadvantage is that cost is too high, affecting its commercialization.

Low energy density, demanding environmental temperatures, and high costs are the main factors that hinder the development of VRFBs. Figure 19 is an outlook and suggestion for the commercial development of VRFBs. The core issue of VRFBs is to improve the energy density of the battery, thus improving its core competitiveness in the field of large-scale storage. The current density of a VRFB is currently between 120 and 150 mA cm<sup>-2</sup> and is expected to reach 400 mA cm<sup>-2</sup> by 2030, which will improve the energy density of the battery as a whole.<sup>167</sup> EE is the standard for evaluating energy conversion efficiency. VRFB EE is weaker than the Li-ion, and its efficiency is less than 80%. Therefore, the EE is stabilized at 75%–85% to help improve the applicable range of VRFB energy storage.<sup>168</sup> Despite VRFB advantages such as high security and stability, the technique of large battery sizes and low energy densities is not suitable for mobile applications. Therefore, the miniaturization of the VRFB stack will be the trend of future development, and the battery volume will be from 1/4 to 1/2 of the conventional stack. In recent years, VRFBs have become more effective and efficient energy storage devices, which can be widely used in power generation sides and user ends (off-grid energy storage, charging station, backup power), and they have broad application prospects in the future.<sup>169</sup>

VRFBs are developing toward a large-scale stationary mode and becoming effective solutions to the intermittent problem of renewable energy generation. Figure 20 is an analysis of the maturation of various energy storage technologies, indicating that the RFB headed by the VRFB is facing opportunities and huge challenges in the energy storage area. Among the many RFBs, VRFB technology is more popular and successful.<sup>170</sup>

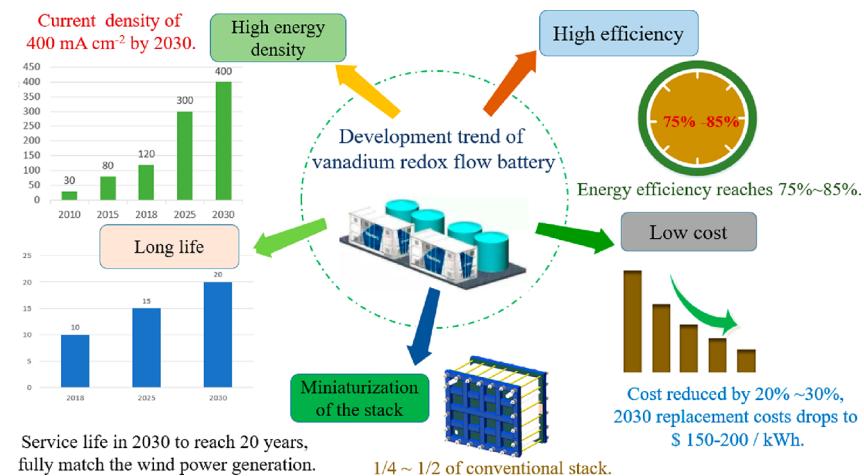
## CONCLUSIONS AND FUTURE PERSPECTIVES

As “carbon peak” and “carbon neutrality” become a global consensus, the proportion of renewable energy in the whole energy system will increase rapidly, and energy storage will usher in explosive growth. Therefore, VRFBs will usher in a huge opportunity. In this work, the shortcoming of VRFB technology and the critical issues affecting its development are reviewed for the first time. Moreover, the difficulties encountered in the commercial development of VRFBs are analyzed and summarized. The factors restricting the development of VRFBs are summarized below into four aspects, and the corresponding analyses are carried out in detail.

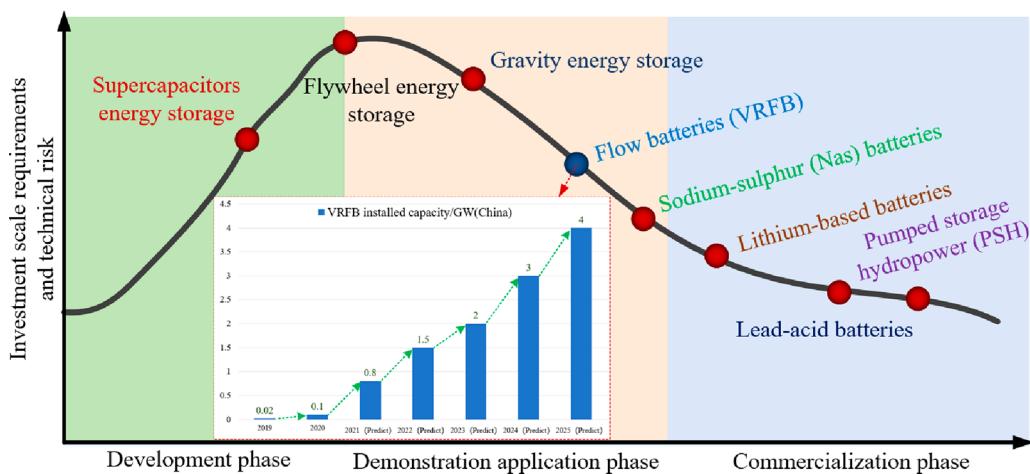
- Electrodes, membranes, bipolar plates, and electrolytes are the key components of VRFBs. Research and development of key materials have the risk of high cost and long cycles, but it is needed to seek further breakthroughs in battery performance. Future research on core materials should consider the differences between single cells, stacks, and modules. The overall performance of the battery system is improved by keeping the material

**Table 5. Main Large-Scale Energy Storage Battery Performance Comparison**

Battery type	Life	Efficiency (%)	Response time	Environmental impact	Discharge capacity	Cost
LAB	Shorter	80	Excellent	Medium	No good	High
NaS	Shorter	70	Excellent	Serious	Good	High
Li-ion	Short	90–100	Good	Medium	Good	High
Cd–Ni battery	Longer	70	Good	Medium	No good	Higher
Metal–air battery	Long	50	General	Better	No good	Low
VRFB	Very long	78	Good	Better	Good	Higher



**Figure 19.** Perspectives of VRFB energy storage systems.



**Figure 20.** Analysis of various storage technology maturations.

- consistency of the single cell and reducing internal resistance and mechanical failure.
- The establishment of a scientific and reasonable battery model can improve the efficiency of research and development and provide scientific and effective theoretical guidance for experimental research and battery structure design. At the same time, it can also provide a theoretical basis for exploring the internal mass transfer law and stable operation of the batteries. At present, VRFBs are being developed toward high performance, and a high-precision model is the premise to achieve this goal. Therefore, it is necessary to establish a hybrid model with multiple physical factors coupled to fully reflect the internal and external characteristics of the batteries.
  - Operation optimization is an effective method to improve battery performance without involving the research and development of key component materials. Among them, the flow field structure design is one of the effective methods for operation optimization, which can realize the uniform flow of electrolytes and efficient and stable operation of the batteries. For this reason, more flow field structure performance should be explored to obtain the law and experience of flow field design. At the same time, the design of the stack needs to consider the inconsistency between cells, electrolyte transfer delay, polarization phenomenon, and other problems.

- At present, the application and promotion of VRFBs are not only affected by their performance but also related to the market mechanism. Therefore, it is necessary to improve the market mechanism and effective incentive measures to further scale and commercialize VRFBs, to reduce the cost of the whole industry, and to increase the competitiveness of VRFBs.

Although the key materials, system modeling, operational optimization, and related theories of VRFBs have achieved significant results, VRFBs are still an attractive research topic. This perspective comprehensively analyzed the bottleneck of VRFB development and will provide good suggestions and references for VRFB research.

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#### Notes

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