Energy Storage Analysis and Flow Rate Optimization
Research of Vanadium Redox Flow Battery

Zebo Huang¹, Anle Mu¹*, Fuxiang Hao¹, Hang Wang¹, and Jianxiang Yang²

1 School of Mechanical and Precision Instrument Engineering, Xi’an University of Technology, Xi’an 710048, China
2 School of Automation, Guangdong Polytechnic Normal University, Guangzhou, 510665, China

Corresponding author: muanle@xaut.edu.cn

Abstract. Vanadium redox flow batteries (VRFBs) have become the best choice for large-scale stationary energy storage technology due to their outstanding advantages such as flexible design, good safety, long life, no ion cross-contamination, and environmental friendliness. The random and intermittent nature of renewable energy has accelerated the promotion and application of VRFBs, which is a promising new energy storage technology. This article briefly discusses the current status and demand of renewable energy power generation, the analysis of the current status of energy storage technology led by VRFBs, the working principle and technical bottlenecks of VRFBs. The focus is on the optimization and design of the flow field structure to improve the distribution characteristics of the electrolyte solution and improve the battery performance. The simulation structure shows that designing a reasonable flow channel size can optimize the electrolyte flow rate and improve performance.

1. Introduction
With the rapid growth of energy consumption and the increase of human demand for energy, the globalization of fossil energy depletion, climate deterioration, air pollution and other issues have become increasingly prominent, making the demand for the promotion and application of renewable energy more urgent. Therefore, changing the way of generating electricity and using renewable energy to generate electricity can effectively solve the environmental damage caused by fossil energy. Renewable energy has a series of advantages such as clean and pollution free, wide distribution, and huge reserves, and it occupies a pivotal position in the future energy structure [1]. In 2019, the world’s newly installed renewable energy capacity reached 176 GW, 90% of which came from photovoltaic (PV) and wind power. It shows that PV and wind power generation have broad prospects. Therefore, it is predicted that by 2050, renewable energy power generation led by wind and PV will account for 48% of the global power structure. Renewable energy will become the dominant global energy source [2]. From 2011 to 2017, the average wind curtailment rate was 13.74%, and the wind curtailment volume reached 26.77 billion kWh. Since 2018, the wind curtailment rate has been well controlled, and will drop to around 5% (22.5 billion kWh) in 2020, but the waste of electricity is still huge.

In order to better introduce renewable energy power generation, the quality and reliability of power supply must be improved. Converting renewable energy power into storable energy and deploying it to the grid in a controlled manner will be an effective solution to the intermittent nature of renewable energy [3]. In order to solve the problem of abandoning wind and PV from renewable energy, improve
the quality of power. Energy storage technology provides effective energy solutions for renewable energy. Realize the power smoothing at the output end of renewable energy, and the grid-connected end [4]. The energy storage module and power module of the VRFB are designed independently of each other, which has high scalability, flexibility and safety. Therefore, it has broad application prospects in the field of large-scale stationary energy storage. However, the low energy density of VRFBs makes the energy storage bulky, which will restrict its promotion and development. The main contributions of this work are: (1) Analyzed the development status of wind energy and PV, and stated the problems (randomness, intermittency and uncontrollability) of renewable energy. (2) Comprehensively analyze the technical characteristics of electrochemical energy storage and select the best energy storage technology. (3) It also pointed out that the VRFB has problems, how to improve its performance and make up for its defects. (4) Aiming at the low energy density of VRFBs, a flow optimization strategy was proposed to improve the overall performance of the battery.

2. Comparison and Analysis of Energy Storage Technology

2.1. Energy storage technology and characteristic analysis
In recent years, renewable energy sources such as wind energy and PV have a huge volume and a rapid growth rate. However, the development of supporting technologies for renewable energy development is lagging, resulting in poor power quality and severe wind curtailment. How to provide the power quality of renewable energy is the focus of energy research. Energy storage technology is one of the top ten disruptive technologies in the future and has broad application prospects in the future. Large-scale stationary energy storage needs to consider five factors such as safety, economy, sustainability, environmental friendliness and high performance. Therefore, it is necessary to comprehensively consider the advantages and disadvantages of energy storage, and select the best energy storage technology to match the corresponding application field[5].

Electrochemical energy storage is the mutual conversion of chemical energy and electrical energy, and is an efficient energy storage technology. It has the advantages of environmental friendliness, fast response time, and considerable energy density. The VRFB is suitable for large-scale stationary energy storage because of its independent power module and energy module and high safety factor. Mainly used in renewable energy power generation, grid peak and frequency modulation and power supply in remote areas. VRFB has typical technical characteristics such as flexible design, easy expansion, no ion cross-contamination, long service life, high safety, good performance, environmental friendliness, and high cost performance. Therefore, VRFB is currently one of the most promising electrochemical energy storage technologies with the largest development space and the most innovative potential [7].

![Figure 1. Schematic diagram of a single VRFB cell.](image-url)

2.2 VRFB system
The VRFB is currently the most mature technology and the most widely used RFB. In the VRFB, the oxidation-reduction reaction of vanadium ions of different valences in the electrolyte occurs on the surface of the electrode to achieve electron entry and de-entrainment. Fig. 1 is a schematic diagram of a
single cell of a VRFB. It consists of battery stacks, electrolyte storage tanks, circulating pumps and other key components, and is connected to distributed power sources, loads and grids through power electronic conversion devices [8]. The VRFB stack is composed of ion-conducting membranes, electrodes, electrode frames, bipolar plates, current collectors, end plates and fasteners. During half-cell positive charging, the \(\text{VO}^{2+}\) lose one electron and oxidizes to \(\text{VO}_2^+\). The discharging process is just the opposite [9]. The potential is 1.004 V.

\[
\text{VO}^{2+} + H_2O - e^- \xrightarrow{\text{charge}} \text{VO}_2^+ + 2H^+ , \quad E_{0+} = 1.004V
\]  

(1)

During half-cell negative charging, the \(\text{V}^{3+}\) gain one electron and reductions to \(\text{V}^{2+}\). Discharge loses an electron and is oxidized. The potential is -0.255 V.

\[
\text{V}^{3+} + e^- \xrightarrow{\text{charge}} \text{V}^{2+} , \quad E_{0-} = -0.255V
\]  

(2)

The overall reaction of the VRFB with porous electrodes is shown in Eq. (3), The overall potential is 1.259 V.

\[
\text{VO}^{2+} \text{V}^{3+} + H_2O \xrightarrow{\text{discharge}} \text{VO}_2^+ + \text{V}^{2+} + 2H^+ , \quad E_{0} = 1.259V
\]  

(3)

2.3 VRFB problem statement

The low energy density of VRFBs is the bottleneck restricting its development and application. How to improve energy density is the focus of research. According to the existing literature, research methods include: (1) Research and development of new materials for key components; (2) Design and optimization of battery structure; (3) Optimization of battery electrolyte flow [11]. The existing literature mainly analyzes how to increase the energy density of the VRFB from the two aspects of developing new component materials and improving the overall performance of the battery. Theoretical analysis shows that optimizing the electrolyte flow rate can improve battery performance and make up for the disadvantage of low energy density [12].

The energy density \(E_{\text{density}}\) expression of vanadium flow battery is as follows:

\[
E_{\text{density}} = \frac{n C_a F V_{\text{dis}}}{m}
\]  

(4)

\[
V_{\text{dis}} = E_{\text{OCV}} - IR_{\text{cell}} - \eta_{\text{act}} - \eta_{\text{con}}
\]  

(5)

where \(n\) is the number of electrons transferred, \(C_a\) is the vanadium ion concentration, \(m\) is the number of electrolyte storage tanks, \(F\) is the Faraday constant, \(V_{\text{dis}}\) is the discharge voltage, \(E_{\text{OCV}}\) is the open
circuit voltage, $I$ is the battery current, $R_{cell}$ is the Ohm resistance, $\eta_{act}$ is the activation polarization, $\eta_{con}$ concentration polarization [13].

Power density is a key factor in evaluating the performance of VRFB. It is proportional to the current density and the average discharge voltage. Under high current density, the electrochemical reaction progresses quickly, reducing charging time. Power density can be calculated in Eq. (6).

$$P_{density} = I_{density} \times \overline{V}_{dis}$$  \hspace{1cm} (6)$$

$$I_{density} = \frac{nFCAQ_p}{A_s}$$  \hspace{1cm} (7)$$

$$Q_p = \frac{i}{nFCaSOC_{min}}$$  \hspace{1cm} (8)$$

where $\overline{V}_{dis}$ is the average discharge voltage, $I_{density}$ is the current density, $Q_p$ is the flow rate, $A_s$ is the electrode area, $SOC_{min}$ is the minimum state of charge[14].

Based on the above problems, the design and optimization of the flow field structure can effectively improve the uniformity of the electrolyte flow, alleviate the concentration polarization, and improve the overall performance of the battery. The flow field structure design methods include: (1) With or without flow channel structure design; (2) Parallel flow channel, interdigital flow channel and serpentine flow channel design and optimization; (3) The same type of flow channel, different flow channel sizes study on the electrolyte flow rate; (4) The electrolyte flow distribution of the same type of flow channel and different cross-sections[15].

This work analyzes the electrolyte flow distribution under different sizes of the serpentine flow channel, comprehensively considers the electrochemical and fluid dynamics factors of the VRFB, and establishes a multi-physics coupling battery model. Fig. 2 is the flow optimization design and analysis process of VRFB[16].

![Figure 2](image_url)

**Figure 2.** Design and analysis process of flow optimization for VRFB, (a) flow field; (b) flow channel; and (b) flow channel size.
3.2 Governing equation

Obtain the key performance parameters of the battery through modeling methods, which can be used to analyze system related problems. Can predict and improve battery performance. This research is based on the equivalent circuit model and establishes a VRFB model with multi-physics coupling including electrochemistry and fluid mechanics. The governing equations are used to describe mass, momentum and charge transfer [17]. The specific expression form of the governing equation is shown in Table 1.

| Governing equations | Specific forms |
|---------------------|---------------|
| Mass conservation equation | $\frac{\partial}{\partial t}(\varepsilon c_i) + \nabla \cdot \vec{N}_i = -S_i$ |
| Darcy’s Law | $\vec{u} = \frac{k}{\mu} \nabla p, \ \nabla p u = 0$ |
| Kozeny-Carman equation | $K = \frac{d^2 \varepsilon}{\kappa_{\text{CK}} (1-\varepsilon)}$ |
| Mass conservation | $\sum_i Z_i c_i = 0$ |
| Membrane kinetics equation | $\dot{N}_{H^+} = -\frac{\sigma_{\text{mem}}}{F} \nabla \phi_{\text{mem}}$ |
| Butler-Volmer equations | $i_{\text{pos}} = A_S F k_{\text{pos}} c_{V^{5+}}^{(1-\alpha_{\text{pos}})} c_{V^{4+}}^{\alpha_{\text{pos}}}$ |
| | $i_{\text{pos}} = i_{0,\text{pos}} \left( \frac{c_{V^{5+}(0,t)}}{c_{V^{5+}}^*} \right) \exp \left( - \frac{\alpha_{\text{pos}} F}{RT} \eta_{\text{pos}} \left( \frac{c_{V^{4+}(0,t)}}{c_{V^{4+}}^*} \right) \exp \left( - \frac{(1-\alpha_{\text{pos}}) F}{RT} \eta_{\text{pos}} \right) \right)$ |
| | $i_{\text{neg}} = i_{0,\text{neg}} \left( \frac{c_{V^{2+}(0,t)}}{c_{V^{2+}}^*} \right) \exp \left( - \frac{\alpha_{\text{neg}} F}{RT} \eta_{\text{neg}} \right) - \left( \frac{c_{V^{2+}(0,t)}}{c_{V^{2+}}^*} \right) \exp \left( - \frac{(1-\alpha_{\text{neg}}) F}{RT} \eta_{\text{neg}} \right) \right)$ |
| Cell voltage equation | $E_{\text{charge}} = E_{\text{OCV}} + IR_{\text{cell}} + \eta_{\text{act}} + \eta_{\text{con}}, E_{\text{discharge}} = E_{\text{OCV}} - IR_{\text{cell}} - \eta_{\text{act}} - \eta_{\text{con}}$ |
| Concentration overpotential | $\eta_{\text{con}} = \eta_{\text{con}}^+ + \eta_{\text{con}}^-$ |
| | $= \frac{RT}{zF} \left( 1 - \frac{i_{\text{pos}}}{zF k_m c_{V^{5+}}^{\text{pos}}} \right) + \frac{RT}{zF} \left( 1 - \frac{i_{\text{neg}}}{zF k_m c_{V^{2+}}^{\text{neg}}} \right)$ |
| Nernst equations | $E_{\text{OCV}} = E_{\text{cell}} + \frac{RT}{zF} \ln \left( \frac{c_{V^{5+}(0,t)}}{c_{V^{3+}} c_{V^{2+}}} \right)$ |
| State of charge (SOC) | $SOC_{\text{theo}} = \frac{C_{V^{2+}}}{C_{V^{2+}} + C_{V^{3+}}} = \frac{C_{V^{5+}}}{C_{V^{4+}} + C_{V^{5+}}}$ |
| Transfer coefficient | $k_m = \alpha v^\beta$ |

where $S_i$ is the source term, $d_f$ is the fiber diameter, $k_m$ is the transfer coefficient, $\alpha$ and $\beta$ are the fitting parameter, $c_i$ is the concentration of species, $D_i$ is the diffusion coefficient, $Z_i$ is the valence of species, $K_i$ is the ionic mobility of species, $\Phi_i$ is the ionic potential, $\vec{u}$ is the electrolyte velocity, $\kappa_{\text{CK}}$ is the Kozeny-Carman constant, $R$ is the molar gas constant, $T$ is the battery temperature, $\varepsilon$ is the electrode porosity, $k_{\text{pos}}$ and $k_{\text{neg}}$ are the positive and negative reaction rate constants, $\alpha_{\text{pos}}$ and $\alpha_{\text{neg}}$
are the positive and negative charge transfer coefficients, $E_{cell}^0$ is the Initial voltage.

The VRFB uses porous electrodes with a sufficiently large specific surface area, so the influence of activation polarization can be ignored. Then the battery voltage during charging is:

$$E_{charge} = E_{cell}^θ + \frac{2RT}{zF} \ln c_{H^+} + \frac{2RT}{zF} \ln \left( \frac{SOC}{1-SOC} \right) + IR_{cell} + \frac{RT}{zF} \left( 1 - \frac{i_{pos}}{zFk_m c_r^{pos}} \right) + \frac{RT}{zF} \left( 1 - \frac{i_{neg}}{zFk_m c_r^{neg}} \right)$$

(9)

The discharge process is the difference between open circuit voltage, ohmic polarization and concentration polarization [18]. The specific expression is as follows:

$$E_{discharge} = E_{cell}^θ + \frac{2RT}{zF} \ln c_{H^+} + \frac{2RT}{zF} \ln \left( \frac{SOC}{1-SOC} \right) - IR_{cell} - \frac{RT}{zF} \left( 1 - \frac{i_{pos}}{zFk_m c_r^{pos}} \right) - \frac{RT}{zF} \left( 1 - \frac{i_{neg}}{zFk_m c_r^{neg}} \right)$$

(10)

where $c_r^{pos}$ and $c_r^{neg}$ are the molar concentrations of the positive and negative reactants respectively; $i_{pos}$ and $i_{neg}$ are the current densities of the positive and negative reactions respectively.

4. Results and discussion

4.1 Cell voltage and overpotential analysis

The performance of a VRFB can be characterized by the battery’s charge and discharge performance parameters. The higher the parameter value, the better the battery performance. The electrolyte flow rate directly affects the electrochemical reaction process of the battery and is closely related to the battery polarization (activation polarization $\eta_{act}$, ohmic polarization $IR_{cell}$, concentration polarization $\eta_{con}$).

In the charging stage as shown in Fig. 3, the smaller the flow rate, the more serious the battery polarization. Therefore, the smaller the flow rate, the higher the battery voltage. There is a phenomenon of false charge, the battery charge is terminated early. During the discharging phase, maintain the same conditions as the charging phase. Due to the influence of concentration polarization, the greater the flow, the closer the battery voltage to the equilibrium potential. Fig. 4 shows the over-potentials of the five channel sizes. The results show that the concentration polarization of the low-velocity battery is serious. As the flow increases, the concentration polarization is relieved, and the battery voltage remains at the equilibrium potential. It can be seen from the figure that the larger the size of the flow channel, the more it deviates from the equilibrium potential [19].

4.2 Influence of flow rate on pressure drop and pump power loss

The pressure drop of the VRFB is the pressure difference between the electrolyte inlet and the outlet, and it is the energy loss during the electrolyte mass transfer process. The pressure drop is proportional to the electrolyte flow rate ($Q$), viscosity coefficient ($\mu$) and pipe length ($l$), and inversely proportional to the mass transfer coefficient ($K$) and the electrode specific surface area ($A$). The pressure drop is defined as follows:

![Figure 3. Charge and discharge voltage curve of VRFB.](image-url)
\[ \Delta p = \frac{\mu l Q}{K A} \]  
\[ P_{pump} = \frac{Q \Delta p}{\varphi_{pump}} \]

where \( P_{pump} \) is the pump power, \( p \) is the pressure, \( \Delta p \) is the pressure drop, \( \varphi_{pump} \) is the pump efficiency.

Figure 4. Overpotential of VRFB.

Figure 5. Pressure drop under different flow channel sizes.

Fig. 5 is the pressure drop analysis of different flow channel sizes at different flow rates. The simulation structure shows that the smaller the size of the flow channel, the greater the pressure drop, and the more energy lost in the electrolyte transmission. The larger the size of the flow channel, the smaller the resistance of electrolyte transmission and the less energy loss. Therefore, as the size of the flow channel increases, the pump power loss becomes smaller, as shown in Fig. 6. The analysis shows that the design of the channel size should consider the electrolyte transport characteristics comprehensively, and choose the best channel size [20].

4.3 Cell efficiency analysis

The electrolyte flow rate has a greater impact on key performance parameters such as coulomb efficiency (CE), voltage efficiency (VE), energy efficiency (EE) and power efficiency (PE) of VRFBs. The metrics in Table 3 are the performance analyze of VRFB[21].

Figure 6. Pump power loss under different flow channel sizes.

Figure 7. Analysis of CE, VE and EE of VRFB.

The smaller the width of the flow channel, the higher the flow rate and the faster the electrochemical reaction. At the same time, the concentration polarization is reduced, and the CE and VE of the battery are high. Fig 7 shows the efficiency distribution of the battery. The five sizes of batteries have high CE, small size and high CE. Compared with the large size, the CE, VE and EE are reduced by 2.0%, 7.0% and 8.4% respectively. Due to the large pressure drop of the small size flow channel, the pump power loss is large. Therefore, the PE of the small-sized flow channel battery is low. As the size increases, the
polarization of the battery becomes serious and the VE is low, resulting in a decrease in PE. A reasonable flow channel design can help improve the electrolyte flow rate and improve the overall performance of the battery [22].

5. Conclusion

VRFB is the most promising electrochemical energy storage in large-scale stationary energy storage. However, the low energy density affects the development of VRFBs. Therefore, by optimizing the electrolyte flow, the overall performance of the battery is improved to compensate for the lack of energy density. The paper analyzes the current status and existing problems of renewable energy development. It is proposed to solve the intermittent problem of renewable energy through the energy storage technology of VRFB. Through the analysis of energy storage technology, it is concluded that the VRFB is very suitable for renewable energy power generation and has a broad application scenario. Because the VRFB has the defect of low energy density, which restricts its development. It is proposed that through the design and optimization of the battery flow field, the flow rate of the electrolyte is increased, the flow resistance of the electrolyte is reduced, the uniformity of the electrolyte distribution is improved, and the overall performance of the battery is finally improved to compensate for the defect of low energy density. The results show that this method can be used for flow optimization and regulation of actual systems. It can improve the uniformity and flow rate of the electrolyte, improve battery efficiency, and reduce energy loss.

6. References

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Acknowledgement

This work was supported by the Ph.D. Innovation fund projects of Xi’an University of Technology (Fund No. 310–252072001) and the National Natural Science Foundation of China (No. 51075326).