Research on performance of vanadium redox flow battery stack

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Abstract. The vanadium redox flow battery is a power storage technology suitable for large-scale energy storage. The stack is the core component of the vanadium redox flow battery, and its performance directly determines the battery performance. The paper explored the engineering application route of the vanadium redox flow battery and the way to improve its energy efficiency, and studied high-power vanadium redox flow battery stack. 10 single cells, half-stack and full stack were assembled and tested for constant current and constant power charge and discharge respectively. The results showed that bipolar plate’s conductive filler was increased, besides, reasonable control of the thickness of the graphite felt could reduce the contact resistance between the materials inside the stack. The internal seal was added in the liquid flow frame to reduce the electrolyte permeability and improve the coulombic efficiency; Increasing the exchange capacity of the ion exchange membrane enhanced the choice of permeability and conductivity. All of the above factors could improve the energy efficiency of the battery. The energy efficiency of the 25kW stack could reach 78.6%, and the 31.5kW stack could reach 76.7%.

1. Foreword
The all-vanadium flow battery energy storage technology has the advantages of high energy conversion efficiency, independent design of power capacity, safe operation, long service life, environmental friendliness and recyclability of electrolyte, and overcomes the environmental protection and safety of other electrochemical energy storage technologies. Such hidden dangers can be used as a supplement to the grid pumped storage peaking device, and has broad application prospects in the fields of new energy access and smart grid construction[1-3].

The stack is the core component of the all-vanadium flow battery energy storage system. The performance of the stack directly determines the performance of the energy storage system[4, 5]. At present, the characterization and test results of all vanadium redox flow battery stacks show that ohmic polarization and activation polarization are the key factors affecting the performance of the reactor. Increasing the electrochemical reactivity of electrode materials is an effective way to reduce the polarization of activation; improving the conductivity of electrodes, bipolar plates, ion-conducting membranes, optimizing the design of stack structure, reducing the internal resistance of the stack is an effective way to reduce ohmic polarization[6, 7]. This paper focuses on the effects of core materials such as bipolar plates, graphite felts, liquid flow frames and ion exchange membranes on battery performance, and explores the engineering application route of all vanadium redox flow batteries and ways to improve their energy efficiency.
2. Experimental part

2.1. Battery assembly

2.1.1. Core material

The influence of core materials such as bipolar plates, liquid flow frames, graphite felts and ion exchange membranes on the performance of high-power, engineered application stacks had been the focus of attention and research. 10 single cells, all-vanadium flow battery half-stack and full stack were assembled[8].

In terms of bipolar plates, two kinds of bipolar plates S1 and S2 were investigated. The graphite felts were mainly investigated for the influence of thickness. Two kinds of graphite felts Z1 and Z2 were studied. For ion exchange membranes, two ion exchange membrane of M1 and M2 were investigated.

| Table 1. Main performance index |
|--------------------------------|
| **Main performance index of bipolar plates** |
| Index name                  | S1                | S2                |
| Thickness(mm)               | 0.78-0.82         | 0.95-1.10         |
| Density(g/cm³)              | ≥1.73             | 0.95              |
| Tensile Strength(MPa)       | ≥36               | ≥50               |
| Bending strength(MPa)       | ≥44               | ≥50               |
| Resistivity(mΩ*cm)          | ≤1.04             | ≤1                |
| Conductivity(S/cm)          | ≥1000             | ≥1000             |

| **Main performance index of graphite felts** |
| Index name | Z1 | Z2 |
| Carbon content(%) | ≥99% | ≥99% |
| Thermal Conductivity(w/m.k) | 0.25 | 0.25 |
| Tensile strength(MPa)   | 0.41 | 0.41 |
| Volumetric weight(g/cm³) | 0.09±0.02 | 0.09±0.02 |
| Ash(%)                  | ≤0.06 | ≤0.06 |
| Thickness(mm)           | 4.2±0.3 | 4.7±0.3 |
| Length(mm)              | Specified length |
| Width(mm)               | Specified length |

| **Main performance index of ion exchange membranes** |
| Index name | M1 | M2 |
| Thickness(μm) | 50 | 100 |
| Moisture content(%) | 5 | 5 |
| Water absorption rate(%) | 50 | 49 |
| Conductivity(S/cm)   | 0.083 | 0.1 |
| Exchange capacity(meq/g) | 0.89 | 0.1 |
| Density               | 1.98 | 1.98 |

The influence of the flow frame is mainly reflected in the design of flow paths, the difference of cover sheets and the presence of internal sealing. Four flow frames K1, K2, K3 and K4 had been
studied[9]. Among them, K1 and K2 used PP cover sheets, K3 and K4 used PVC cover sheets; K2 flow paths were shown in Fig. 1(a), and the other three flow paths were shown in Fig. 1(b). The flow path 1 was a single flow path structure, the flow path 2 increased the number of flow paths, changed the flow path direction, and the inner seal strip was added in the K4 flow frame, the other three had no inner seal.

2.1.2. Assembly process
In the assembly process of the stack, the assembly sequence of the battery components such as the end plate, the copper plate, the bipolar plate, the graphite felt, the liquid flow frame and the ion exchange membrane was designed, single cell and stack structure were improved.

The design of the positioning hole and the positioning rod was used to realize the matching and positioning of the battery assembly, the fixing and compacting of the battery were performed by using the screw, the positioning and fixing process was improved by the combination of the manual and the machine, and the compression and sealing means of the electric pile were improved. 10 single cells, half stack (30 single cells) and a full vanadium redox flow battery stack (60 single cells) were assembled.

After the battery assembly was completed, quality control was performed using detection steps such as thickness detection and water circulation test.

2.2. Test methods
After the battery assembly was completed, it was subjected to a water cycle test for 5 hours to verify the sealing performance of the battery. Then, the battery module test system was used to test the 10 single cells, vanadium redox flow battery half stack and full stack. The constant current and constant power tests were used to investigate the energy efficiency, coulombic efficiency, charge and discharge performance and stability of all vanadium redox flow batteries.

3. Results and discussion

3.1. Study on performance of 10 single cells

3.1.1. Effect of bipolar plate
The effect of bipolar plates on the performance of single cells was investigated. Two kinds of 10 single cells were assembled, and two kinds of bipolar plates S1 and S2 were respectively used to conduct constant current charge and discharge tests on the single cells. The results are shown in Table 2.
Table 2. Number 1 and 2 10 single cells’ charge and discharge performance

| Battery number | Bipolar plate | Coulomb efficiency | Voltage efficiency | Energy efficiency |
|----------------|---------------|---------------------|--------------------|-------------------|
| 100A Constant current | | | |
| 1 | S1 | 80.78% | 92.8% | 74.96% |
| 2 | S2 | 79.86% | 92.94% | 74.23% |
| 200A Constant current | | | |
| 1 | S1 | 87.33% | 85.09% | 74.34% |
| 2 | S2 | 85.39% | 86.48% | 73.84% |

It can be seen from the results of the charge and discharge test that the 10-cell cells using the S1 bipolar plate have higher coulombic efficiency and energy efficiency. Comparing the parameters of two bipolar plates, the mechanical strength of S1 is slightly worse than that of S2. The S1 is thinner and the density is significantly larger. Composite bipolar plates are usually made of conductive fillers and polymer resins. They have good mechanical strength and processing properties of polymer resins and excellent electrical conductivity of conductive fillers.

The important indicators affecting the performance of bipolar plates are usually resistivity and mechanical properties. S1 is thinner and denser, indicating that a larger proportion of conductive filler is added to ensure the mechanical strength required for engineering applications. The addition of a conductive filler helps to reduce the electrical resistivity of the bipolar plates.

3.1.2. Effect of graphite felt

The effects of graphite felt on the performance of single cells were studied. Two kinds of 10 single cells were assembled. Two kinds of graphite felts, Z1 and Z2, were used to charge and discharge the single cells. The results are shown in Table 3.

Table 3. Number 3 and 5 10 single cells’ charge and discharge performance

| Battery number | Graphite felts | Coulomb efficiency | Voltage efficiency | Energy efficiency |
|----------------|---------------|---------------------|--------------------|-------------------|
| 200A Constant current | | | |
| 3 | Z1 | 89.86% | 85.64% | 76.96% |
| 5 | Z2 | 89.36% | 87.65% | 78.32% |
| 300A Constant current | | | |
| 3 | Z1 | 90.86% | 80.07% | 72.75% |
| 5 | Z2 | 89.83% | 83.28% | 74.81% |
| 340A Constant current | | | |
| 3 | Z1 | 91.39% | 77.49% | 70.82% |
| 5 | Z2 | 89.28% | 81.93% | 73.4% |

It can be seen from the test results that after using the Z2 graphite felt, the voltage efficiency and energy efficiency of the single cell are significantly improved. Comparing the index parameters of the two graphite felts, the Z2 graphite felt is thicker (4.2 mm) than the Z1 except for the thickness (4.7 mm), and there is no difference in other parameters.

Research on graphite felts shows that the use of surface metallization, acid treatment, heat treatment, electrochemical treatment, ammoniation and other modification techniques can improve the electrochemical performance of graphite felt by increasing the surface area, increasing the number of surface oxygen-containing functional groups and reducing the electrical resistance[10].

In this paper’s study, the thickness of the graphite felt increased, the compression of the graphite
felt was increased to about 20%, the contact resistance was lowered, and the battery performance was improved without affecting the mechanical strength and other properties.

3.1.3. Effect of liquid flow frames
The effect of the flow frame on the performance of the single cell was studied. Three 10 single cells were assembled using three flow frames K1, K2, and K3, and constant current and constant power charge and discharge tests were performed. The results are shown in Table 4.

| Battery number | Liquid flow frames | Coulomb efficiency | Voltage efficiency | Energy efficiency |
|----------------|--------------------|---------------------|--------------------|-------------------|
| 4              | K1                 | 91.19%              | 88.3%              | 80.52%            |
| 5              | K2                 | 89.36%              | 87.65%             | 78.32%            |
| 6              | K3                 | 91.31%              | 87.05%             | 79.49%            |

200A Constant current

| Battery number | Liquid flow frames | Coulomb efficiency | Voltage efficiency | Energy efficiency |
|----------------|--------------------|---------------------|--------------------|-------------------|
| 4              | K1                 | 91.67%              | 83.45%             | 76.5%             |
| 5              | K2                 | 89.83%              | 83.28%             | 74.81%            |
| 6              | K3                 | /                   | /                  | /                 |

300A Constant current

| Battery number | Liquid flow frames | Coulomb efficiency | Voltage efficiency | Energy efficiency |
|----------------|--------------------|---------------------|--------------------|-------------------|
| 4              | K1                 | 91.7%               | 81.49%             | 74.61%            |
| 5              | K2                 | 89.28%              | 81.93%             | 73.4%             |
| 6              | K3                 | 94.92%              | 81.11%             | 76.98%            |

340A Constant current

| Battery number | Liquid flow frames | Coulomb efficiency | Voltage efficiency | Energy efficiency |
|----------------|--------------------|---------------------|--------------------|-------------------|
| 4              | K1                 | 91.35%              | 82.15%             | 75.04%            |
| 5              | K2                 | /                   | /                  | /                 |
| 6              | K3                 | 93.02%              | 83.32%             | 77.5%             |

4.2kW Constant power

It can be seen from the test results that the K2 flow frame has the worst effect, and the single cell has the highest energy efficiency after using the K3 flow frame. The comparison shows that the PVC cover sheet is superior to the PP cover sheet, and the structure of the flow path 2 is also superior to the flow path 1. The study examined the effect of the inner seal on the performance of the cell in the cell path. Two 10 single cells were assembled by means of no inner seal (K3 flow frame) and internal seal (K4 flow frame), constant current and constant power charge and discharge tests were performed. The results are shown in Table 5.

| Battery number | Liquid flow frames | Coulomb efficiency | Voltage efficiency | Energy efficiency |
|----------------|--------------------|---------------------|--------------------|-------------------|
| 7              | K3                 | 92.18%              | 83.46%             | 76.93%            |
| 8              | K4                 | 95.68%              | 81.86%             | 78.32%            |

340A Constant current

| Battery number | Liquid flow frames | Coulomb efficiency | Voltage efficiency | Energy efficiency |
|----------------|--------------------|---------------------|--------------------|-------------------|
| 7              | K3                 | 93.61%              | 79.07%             | 74.01%            |
| 8              | K4                 | 96.51%              | 80.23%             | 77.43%            |

408A Constant current

| Battery number | Liquid flow frames | Coulomb efficiency | Voltage efficiency | Energy efficiency |
|----------------|--------------------|---------------------|--------------------|-------------------|
| 7              | K3                 | 88.3%               | 84.96%             | 75.02%            |

4.2kW Constant power

Table 5. Number 7 and 8 10 single cells’ charge and discharge performance
It can be seen from the test results that the Coulomb efficiency and energy efficiency are greatly improved after the internal flow strip is added to the flow path. After the inner seal is added in the liquid flow frame, the effective area of electrolyte in the flow path is improved, the electrolyte permeability is lowered, the coulombic efficiency is improved, and the overall charge and discharge performance of the battery is improved.

### 3.1.4. Effect of ion exchange membrane

The effects of different ion exchange membranes (separators) on the performance of single cells were studied. Through the previous screening and comparison, the M1 and M2 ion exchange membranes were compared. Constant current and constant power charge and discharge tests were carried out respectively, and the results are shown in Table 6.

#### Table 6. Constant current charging and discharging performance of No. 8 and No. 9 single cells

| No. | Ion exchange membrane | Coulomb efficiency | Voltage efficiency | Energy efficiency |
|-----|-----------------------|---------------------|--------------------|-------------------|
|     | 340A Constant current |                     |                    |                   |
| 8   | M1                    | 95.68%              | 81.86%             | 78.32%            |
| 9   | M2                    | 94.89%              | 82.09%             | 77.89%            |
|     | 408A Constant current |                     |                    |                   |
| 8   | M1                    | 96.51%              | 80.23%             | 77.43%            |
| 9   | M2                    | 94.92%              | 78.46%             | 74.47%            |
|     | 425A Constant current |                     |                    |                   |
| 8   | M1                    | 96.84%              | 77.83%             | 75.37%            |
| 9   | M2                    | 95.02%              | 76.56%             | 72.74%            |
|     | 4.2kW Constant power  |                     |                    |                   |
| 8   | M1                    | 95.02%              | 82.71%             | 78.58%            |
| 9   | M2                    | 93.92%              | 81.83%             | 76.86%            |
|     | 5.1kW Constant power  |                     |                    |                   |
| 8   | M1                    | 96.82%              | 79.83%             | 77.29%            |
| 9   | M2                    | 95.58%              | 78.31%             | 74.83%            |
|     | 5.3kW Constant power  |                     |                    |                   |
| 8   | M1                    | 97.51%              | 78.41%             | 76.46%            |
| 9   | M2                    | 94.81%              | 77.36%             | 73.34%            |

It can be seen from the test results that the vanadium battery of M1 ion exchange membrane has better application performance. Comparing the parameters of the two membranes, the thickness of M1 is half of M2, the exchange capacity is much higher than M2, and other parameters are consistent. The exchange capacity is a key parameter of the ion exchange membrane. The exchange capacity of the membrane is high, the permeability is selected, the conductivity is strong, and the battery performance is better.

### 3.2. Study on performance of half all vanadium redox flow battery stack

Based on the summary of raw materials, components and assembly processes of all vanadium redox flow cells in the previous section, the performance and testing of half stacks were carried out. In this part of the study, the bipolar plates, graphite felts and ion exchange membranes were all those with superior performance in the previous single cell study. Focusing on the influence of the liquid flow frame, two half stacks No. 1 and No. 2 were assembled by K3 and K4 flow frames respectively, and the constant current and constant power tests were carried out. The results are shown in Table 7.
It can be concluded from the test results that the K3 flow frame shows the best performance of the battery among three liquid flow frames K1, K2 and K3. And the performance of K3 in the half stack is still better than K4.

3.3. Study on performance of full all vanadium redox flow battery stack
Based on the study of single cells and half-stacks, we tried to assemble the full stack and used the bipolar plates, graphite felt and liquid flow frame with excellent performance in the previous study. The effects of ion exchange membranes were mainly investigated. The full stack No. 1 and No. 2 were assembled by M1 and M2 ion exchange membranes, and constant current and constant power tests were carried out. The results are shown in Table 8 and Table 9.

Table 7. Number 1 and 2 half stacks’ charge and discharge performance

| Battery number | Liquid flow frames | Coulomb efficiency | Voltage efficiency | Energy efficiency |
|----------------|-------------------|--------------------|--------------------|------------------|
| 272A Constant current | | | | |
| 1 | K3 | 90.4% | 85.7% | 77.5% |
| 2 | K4 | 88.1% | 87% | 76.6% |
| 340A Constant current | | | | |
| 1 | K3 | 91.6% | 84.5% | 77.4% |
| 2 | K4 | 89.4% | 85.1% | 76% |
| 408A Constant current | | | | |
| 1 | K3 | 93.2% | 80% | 74.5% |
| 2 | K4 | 91.2% | 81.3% | 74.1% |
| 12.75kW Constant power | | | | |
| 1 | K3 | 91.8% | 84% | 77.1% |
| 2 | K4 | 88.8% | 85.5% | 75.9% |

The constant power test results of the No. 1 full stack show that the high-power stack can achieve nearly 80% energy efficiency in the charging and discharging process, which has a relatively large application prospect and potential in practical applications. It can be seen that the performance index of stack’s core materials is closely related to the stack’s charge and discharge performance including energy efficiency and voltage efficiency, and the large power stack still has large performance improvement space.
Table 9. Number 1 and 2 full stacks’ charge and discharge performance

| No. | Ion exchange membrane | 31.5kW Constant power |  
|     |                        | Coulomb efficiency | Voltage efficiency | Energy efficiency |
|-----|------------------------|--------------------|--------------------|-------------------|
| 1   | M1                     | 93.8%              | 81.8%              | 76.7%             |
| 2   | M2                     | 95.6%              | 77.5%              | 74%               |

As can be seen from the comparison, the stack using the M1 ion exchange membrane is slightly more energy efficient than the stack using M2 ion exchange membrane. The M1 ion exchange membrane still exhibits better battery performance than M2 in the full stack.

4. Conclusion
By studying the effects of raw materials on the charge and discharge performance and stability of all vanadium redox flow batteries, the assembly process of high power stacks was explored. The content of conductive filler in the bipolar plate increases, the resistivity decreases. The thickness of the graphite felt increases, the compression amount is increased and the contact resistance is lowered. The inner seal is increased in the liquid flow frame, increase the effective contact area of the electrolyte, the Coulomb efficiency, and reduce the permeability. The exchange capacity of the ion exchange membrane is increased, and the selective permeability and conductivity are improved.

All of the above changes can improve the energy efficiency as well as charge and discharge performance of the battery.

In the key technology research and engineering development of stacks, the mass transfer uniformity of the stack and the structure of the stack, the design of the stack structure and the engineering development technology, the key material characteristics of the stack and the impact on the performance of the stack are essential factors for attention and research. In the research of key technologies of the stack forming process, the influence of the stack forming process’s parameters on the stack’s performance as well as the quality control technology of the stack forming will also become the focus of attention in the future.

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References
[1] F M Meng, J. Tera. Sci. Elec. Info. Technol, 2(1997)
[2] H M Zhang, New. Eng. Vehicle. Weekly, 017(2018)
[3] J Noack, N Roznyatovskaya, T Herr, et al, Angew. Chem. Int. Ed, 54(2015)
[4] X L Wang, Y Zhang, Y Li, et al, Energy. Storage. Sci. Technol, 4(2015)
[5] J Ma, A K Li, B Dong, et al, Chin. J. Power Sources, 37(2013)
[6] C X Xie, Q Zheng, X F Li, et al, Energy. Storage Sci. Technol, 6(2017)
[7] J Ma, A K Li, X J Yang, et al, Chin. J. Power Sources, 36(2012)
[8] T Du, X D Liao, Z X Hao, et al, Chin. J. Power Sources, 37(2013)
[9] N Liu, A K Li, Chem. Ind. Eng. Prog, 36(2017)
[10] T Du, A K Li, F Liu, et al, Chin. J. Power Sources, 37(2013)