Measures to Improve The Vanadium Flow Battery

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Abstract. As a kind of emerging energy storage measure, the vanadium flow battery utilizes the ion exchange of vanadium ions to store and discharge energy. Among the existing energy storage technologies, it has high potential and significance due to its several advantages. However, there are still aspects that can be improved and promoted: in battery diaphragm, the voltage and current efficiency could be improved by modifying the ion permeability; The cost of electrolyte is high which can still optimize by selecting low-cost material, through mixing the electrolyte, the cycle life can be extended as well as enable the discharge capacity regeneration; Electrode has the problem of corrosion that affects the lifetime of an electrode, meanwhile, reduce the battery efficiency. In this article, the research progress of vanadium flow battery and the defective aspects of it is investigated, and based on the available cases, the possible solutions and suggestions for the existing problems in battery cells, electrolytes, and electrodes are analyzed. At last, the overall prospect of the vanadium flow battery itself is also discussed.

Keywords: Vanadium flow battery; electrode electrolyte; membrane.

1. Introduction

Since the 21st century, the problem of energy shortage has become really serious. At the same time, the large amount of greenhouse gas emissions have caused very serious damage to the global ecological environment. The UK has proposed zero carbon emissions by 2050, which is important to achieve by getting rid of conventional energy. Last year, energy shortages and greenhouse effects had a serious negative impact on some European countries. In the summer, high temperatures have a serious impact on people's lives and health. In the winter, war leads to a sharp rise in energy prices and people cannot afford high bills. As a result, the government has had to develop renewable energy sources to get rid of its dependence on traditional energy sources. However, as the power generation of renewable energy such as wind, tidal and solar power varies by year in time and geographical location, it also has a negative impact on the power grid and cannot meet the local supply and demand relationship. Therefore, it is important to improve this situation by using energy storage devices. In recent years, mobile batteries have attracted wide attention because of their reliability, ease of design, environmental friendliness, and high safety advantages so that they can be deployed on a large scale.

Under the current technical level, the initial investment cost of vanadium battery is indeed higher than that of lithium battery. This is due to the vanadium battery industry is just emerging, although the industrial chain is basically perfect, but the due scale has not been reached. However, no matter from the perspective of battery material or core reactor, vanadium battery still has a lot of room for improvement, and vanadium battery still has the potential of a large technology to reduce the cost. The cost of the electrolyte accounts for about 70% of the cost of the whole energy storage system. Because electrolyte can be recycled and does not need to be scrapped, the price of its life cycle is low and its economic performance is good. After the battery system is scrapped, vanadium battery can be recycled in addition to the electrolyte, but also other metal materials and carbon materials can also be effectively used without polluting the environment. If increased production, vanadium flow battery still has a lot of room for development in terms of performance and cost control. More importantly, in low or extremely high temperatures, vanadium flow batteries are more safe and more reliable than lithium batteries or lead-acid batteries, which can meet certain specific needs on the market.

At present, such energy storage battery can be mainly used in a variety of fields, such as: 1. Emergency backup power supply in the community or hospital; 2. power supply centers in rural or remote areas where lines are not easy to be laid; 3. Supplementary power supply for areas such as solar or wind energy, which cannot sustain power supply. This review will review current vanadium flow batteries to overcome in large-scale applications. This review will introduce membranes, electrolytes and electrodes, and how these components can be optimized for better system performance.

2. Progress of diaphragm research

2.1. The introduction of diaphragm

The diaphragm in the flow battery is an ion conduction membrane located in the center of each cell and is used to separate the electrolyte from the negative electrode within the cell to prevent the active materials from the meeting, reacting and discharging. Diaphragm is an important part of a liquid flow battery. The function of the diaphragm is to isolate vanadium ions and conduct hydrogen ions, thus enabling ion conduction in the circuit. More importantly, the permeability, stability and production cost of the diaphragm the important factors affecting the large-scale application of flow batteries.

2.2. Type of diaphragm

There are two main types of diaphragm materials: screening membrane (including fluorinated and non-fluorinated materials) and proton exchange membrane (perfluorinated sulfonic acid membrane)[1]. At present, there is no particularly mature diaphragm type, and most studies still use ion exchange to achieve migration of hydrogen ions on both sides of the membrane by the principle of ion exchange. Ion-exchange membranes are usually composed of a polymer backbone, fixation groups, and dissociation ions. ions are connected with fixed groups by electrostatic gravity and can be exchanged with ions of the same charge in the external environment of the membrane, thus enabling current conduction within the membrane. According to the properties of dissociation ion in the material, the diaphragm of vanadium battery can be divided into three categories: 1. cation exchange membrane (dissociation ion is cation); 2. Anion exchange membrane (dissociation ion is anion); 3. Zwitterion exchange membrane (neutral membrane containing both negative and Yang dissociation ions). Among them, the zwitterion exchange membrane is the focus of current research because it has the characteristics of negative and cation exchange membranes and has a good application prospect.

2.3. The research in diaphragm

The diaphragm of vanadium flow battery usually has the following characteristics: 1. The high permeability of hydrogen ions and the small diaphragm resistance, which is conducive to improving the voltage efficiency; 2. The low permeability of vanadium ions, reduces the chance of active substances to meet and discharge, thus improving the current efficiency; 3. With the characteristics of chemical corrosion resistance and electrochemical oxidation resistance, it can ensure that the diaphragm has a long life; 4. The water permeability of battery charging and discharge is small, and it is easy to realize the water balance of positive electrode and negative electrode electrolytes. At present, the well-known cation exchange membrane is Nafion membrane. The cation exchange membrane has more than 90% voltage efficiency and good conductivity. The membrane molecular formula is shown in Figure 1 below. If the thickness of the Nafion film is increased, the vanadium ion permeability can be reduced and the efficiency of the battery can be improved, but the cost is increased. In situ polymerization of styrene sulfonic acid and styrene copolymer into the cation exchange membrane prepared by the bacterial cellulose skeleton can increase the density of the exchange membrane. After 200 charge and discharge cycles, the Coulomb efficiency remains above 99%, but the stability of the inner cell membrane is reduced [2]. Polystyrene polyvinylidene fluoride can be used to produce a cation exchange membrane with a semi-interpenetrating network structure by thermoplasticity of a heterogeneous membrane, which will be better than the comprehensive performance of the existing heterogeneous membrane in China(See Figure 1) [2].

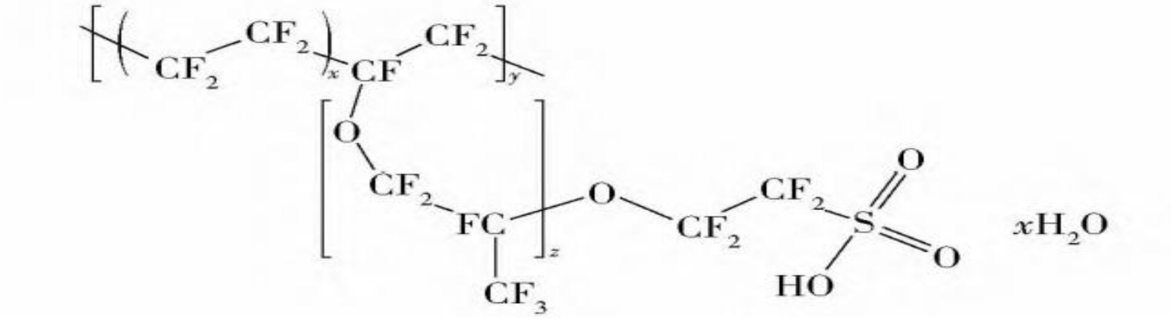

Figure 1. Molecular structure of Nafion membrane

3. The research progress of vanadium flow battery electrolyte

3.1. The introduction of electrolyte

Flow batteries employ two different electrolyte solutions that flow through two different compartments and are divided by a membrane. They are rechargeable electrochemical energy storage devices. The performance and efficiency of the flow battery are greatly influenced by the characteristics and structure of the electrolyte, and careful consideration and optimisation of these aspects are necessary to create efficient and dependable energy storage systems. Due to their low cost and excellent ionic conductivity, aqueous electrolytes are the most often utilised kind in flow batteries. They typically comprise of acidic or basic water-based solutions of metal ions like vanadium, iron, or zinc. On the other hand, nonaqueous electrolytes employ organic solvents, have greater energy densities, but are often more costly and have poorer ionic conductivity. To enhance their functionality and lifespan, electrolytes may also include additives and stabilisers in addition to the ions and solvents that are utilised. The performance and efficiency of flow batteries are largely influenced by the kind and structure of the electrolyte [3]. A VFB's electrolyte typically consists of vanadium ions in a mixture of sulfuric acid and a reducing acid, like hydrochloric acid or sulfuric acid. Vanadium ions may reversibly interconvert between their two oxidation states, +5 and +4, while they are being charged and discharged. As a result, the characteristics of the electrolyte have a significant impact on the performance of VFBs.

The electrolyte concentration affects the battery's capacity and energy efficiency because contaminants in the electrolyte deplete vanadium ions. Researchers have looked into a number of techniques to clean the electrolyte and get rid of contaminants including iron, nickel, and chromium. For instance, metal ions may be removed from electrolytes using ion exchange resins, producing high-purity electrolytes with exceptional stability and performance. Nevertheless, an excessive amount of vanadium in the electrolyte can reduce the efficiency and stability of the battery and increase the energy density of VFBs by causing greater viscosity and vanadium crossover. Sulfates, phosphates, and carboxylic acids were utilised as additives by the researchers to adjust vanadium ion concentration and enhance VFB performance.

3.2. Electrolyte mixing in vanadium flow batteries

The hybrid approach not only has significant benefits in extending the battery cycle but also provides the same or better average discharge capacity per cycle. The appropriate time for mixing can be determined by considering maintenance frequency and discharge capacity requirements. For extensive energy storage, VFB is the best option. The concentration of vanadium ions in the electrolyte can be raised after electrolyte optimisation, resulting in a larger energy density and improved electrochemical performance. Redox kinetics, Coulombic efficiency, and energy efficiency are a few additions that can boost an electrochemical system's performance. Because vanadium ions are more soluble in mixed electrolytes and the batteries are more stable, the energy density of VFBs is further increased[4].

3.3. Using mixed acid solution as supporting electrolyte

Acids that are mixed together often include sulfuric and hydrochloric acids. Vanadium ions become more soluble in the electrolyte when hydrochloric acid is added to the sulfuric acid electrolyte, increasing battery capacity and energy output. The operational temperature range of the VFB can also be increased by using a mixed-acid electrolyte since the hydrochloric acid decreases the electrolyte's viscosity at lower temperatures and raises its ionic conductivity. The mixed-acid electrolyte can improve the stability of VFBs and lessen the possibility of adverse side effects in addition to increasing the solubility of vanadium ions. The precipitation of vanadium ions, which can result in ineffective batteries and subpar performance, is less likely to occur when chloride ions are present in the electrolyte[5].

In conclusion, the performance and stability of all-vanadium redox flow batteries are significantly influenced by the electrolyte. To increase the effectiveness and stability of VFBs, recent research has concentrated on creating high-purity electrolytes, managing vanadium concentrations, and optimising additives. These developments are essential for the creation of large-scale VFB energy storage systems and support the shift to a future with more environmentally friendly energy sources.

4. The research progress of vanadium flow battery electrodes

4.1. Corrosion

Electrode is an essential part to form a vanadium flow battery, it provides space for the redox reaction. The electrodes are divided into positive electrodes and negative electrodes, respectively going through a redox reaction within the catholyte and anolyte. Nowadays, the three main types of electrodes for vanadium flow batteries are carbon electrodes, metal electrodes, and composite electrodes. According to the current researches on vanadium flow battery electrodes, one of the biggest problems currently is corrosion, also called degradation. Corrosion can decrease the performance and lifespan of the flow battery, which could be caused by several factors including heat, chemical reaction, mechanical degradation, and chemical aging [6]. The corrosion is related to the material of the electrodes. Currently, the most common electrode materials are graphite and carbon felt, however, corrosion still could be happened to both two substances under specific circumstances, and different materials used in positive or negative electrodes may also lead to corresponding corrosion.

4.2. Corrosion analysis

To understand the impact of corrosion on vanadium flow battery electrodes, the analysis will be based on the four main types of electrode corrosion: electrochemical corrosion, mechanical corrosion, heat corrosion, and chemical aging [6].

4.2.1 Electrochemical corrosion

The carbon felt and graphite electrodes have high electrical conductivity and stability, low cost, meanwhile are acid resistant. Therefore, they have been widely applied in recent years [7]. Nevertheless, those two electrodes are susceptible to corrosion as positive electrodes due to the $CO2$ evolution, which is caused by the chemical reaction. Such corrosion can degrade the battery's performance, in severe cases, it may even cause battery systems to malfunction. Meanwhile, for the negative electrode, a Hydrogen evolution might take place as well, which can strongly affect the negative electrode by deconstructing the carbon fiber structure.

During the process of the battery being charged, the oxygen evolution will happen on the positive electrode and attach to the surface of it. It then reacts with the carbon structure of the positive electrode and forms CO2, which shows in figure 1, and the hydrogen evolution in figure 2 goes through a similar process, except it takes place in the negative electrode. In general, it's known that an oxygen evolution will reduce the thermal conductivity of the electrode, while the hydrogen evolution can cause the decrease of charge transport coefficient, and both of them can block the flow of electrolytes to decrease the battery performance [6].

4.2.2 Mechanical corrosion

This kind of corrosion almost merely happens in carbon cloth electrodes due to the small surface area and the special flow-by operation of it [6-8]. Those factors will largely increase oxygen evolution by limiting vanadium ion diffusion, hence, it leads to a high mechanical corrosion rate. Because high mechanical corrosion is almost unable to be avoided in carbon cloth electrodes, it is not widely applied or researched. Such corrosion will lead to the active surface loss of the electrode, and make the pores be blocked [8].

4.2.3 Thermal corrosion

Thermal corrosion is caused by the thermal differentiation within the electrode. In a Carbon electrode, the such temperature difference will then cause the carbon to expand. Meanwhile, the thermal difference could also affect the chemical reaction. The heat itself can also trigger the malfunction of the electrode [6, 8]. However, about the phenomenon above, several other inducements instead of corrosion could also trigger them. Meanwhile, researchers still know little about the thermal corrosion aspect. In this way, there is no way to determine whether thermal corrosion could be the primary cause [8].

4.2.4 Chemical aging

This kind of corrosion is almost inevitable to all carbon fiber electrodes, which undoubtedly include carbon felt and graphite electrodes. The principle of the causation is the vanadium and sulfuric acid within the electrolyte can react with the carbon, and such a chemical reaction causes chemical aging. According to the research, chemical aging could generate oxygen functional groups, and damage the electrode performance through oxidation. In addition, compared with the positive electrode, chemical aging could cause greater damage to the negative electrode [6, 9].

4.3. Suggestions

From the analysis, the four major existing corrosion problems are provided and defined. In response to the problems mentioned above and their possible causes, some solutions will be given for solving the problem. For the 4.2.3 thermal degradation part, the current research progress of it is not in-depth, the suggestion for that part will be skipped.

4.3.1 Higher electrochemical stability

Electrochemical corrosion is mainly due to the chemical reactions that are caused by the oxygen and hydrogen evolution, which is hard to handle. However, starting from another perspective, the corrosion could be mitigated by making the electrode material more electrochemical stable. In this way, it could be modified by adding more surface functional groups through the surface deposition of some catalysts. Meanwhile, an artificial rayon carbon felt could be an appropriate substitute. After an experiment that a single battery cell charged and discharged over 2000 times, comparing the artificial rayon carbon felt electrode with the graphite electrode, it has significantly higher electrochemical stability [7].

4.3.2 Modified carbon cloth

Mechanical corrosion usually happens in carbon cloth electrodes instead of the electrode types that use other materials. But to sinter normal preprocessing carbon cloth under the temperature between 600 Celsius to 650 Celsius, a modified carbon cloth will be made. It has good penetration, which is also been widely used and investigated in recent years [7].

4.3.3 Improvement of the negative half battery material

Chemical aging is caused by the chemical reaction which happened when the components within the electrolyte such as vanadium react with the carbon of the electrode. Inside the electrolyte, the existence of vanadium is inevitable, while the material of the electrode itself could be improved, however. According to Gencten and Sahin, titanium dioxide (TiO_2) could restrain the damage caused by oxygen evolution and enhance the reversibility of oxidation reactions [10]. By modifying the electrode using TiO_2 could reduce the negative effect of chemical aging.

5. Conclusion

Although vanadium flow batteries have strong potential for future development, there are still a number of issues that need to be addressed, such as the low energy density, the environmental damage caused by the electrolyte and the high cost of the liquid flow battery, all of which have an impact on the large-scale use of flow batteries. The next step is to increase research into electrolyte, membrane and electrode materials. The next step is to increase research into electrolyte, membrane and electrode materials to improve the performance, stability and overall efficiency of liquid flow batteries and to use modelling and other tools to optimise the design of flow batteries.

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