Liquid Flow Batteries: Principles, Applications, and Future Prospects

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Abstract. This paper aims to introduce the working principle, application fields, and future development prospects of liquid flow batteries. Fluid flow battery is an energy storage technology with high scalability and potential for integration with renewable energy. We will delve into its working principle, main types, advantages and limitations, as well as its applications in power systems and industrial fields. In addition, we will also discuss current research directions and future development trends in order to provide a comprehensive understanding of liquid flow battery technology. And this technology is an advanced electrochemical energy storage technology that has garnered significant attention in the fields of renewable energy integration, energy reserves, and grid stability. Unlike conventional solid-state batteries, liquid flow batteries derive their name from the use of liquid electrolytes for energy storage. Nonetheless, liquid flow batteries face some challenges. However, ongoing technological advancements hold the promise of liquid flow batteries becoming a prominent solution for renewable energy storage in the future, contributing significantly to clean energy and sustainable development.

Keywords: Flow battery, Lithium battery, Electrode, Electronic devices.

1. Introduction

Energy plays a crucial role in supporting global economic growth by driving industrial, transport, and agricultural activities. However, current energy consumption heavily relies on non-renewable fossil fuels, including oil, natural gas, and coal, which are facing severe depletion challenges. Liu's research revealed that China ranked top in the world in energy consumption in 2012, with a 20.3% share, and has a high dependency ratio on fossil fuels [1].

To tackle with the energy crisis, various renewable energy reservation methods are brought into everyday life, including the use of molten salt and solar ponds to store thermal energy, and batteries, such as supercapacitors, Li-ion, Na-S, and Lead-acid batteries, for electrochemical energy storage.

Thus, renewable energy sources, such as electricity, are gradually replacing non-renewable resources [2]. For example, China has developed the most advanced hydrogen fuel cell, indicating that batteries are gradually replacing non-renewable energy sources, such as oil and coal [3]. Power system and renewable energy integration has long been hampered by the need for energy storage. Lithium-ion batteries are an example of a traditional energy storage technology that works well in small-scale applications but has limited scalability and longevity. In this regard, research and interest in liquid flow batteries as an energy storage technology have increased. Liquid flow batteries have the ability to separate and store chemical and electrical energy, making them highly scalable, long-lasting, and flexible.

2. Working Principle and Key Components of Liquid Flow Batteries

Liquid flow battery is an electrochemical energy storage system based on two flowable electrolyte solutions located in two independent storage tanks, as shown in fig.1. These two electrolyte solutions exchange through a set of electrochemical reactions, generating electrical energy. A liquid flow battery typically consists of two electrodes, an anode and a cathode, each in contact with two different electrolytes. When the battery is charged, the external power supply inputs electrical energy into the

system, separating the electrolyte. When the battery is discharged, the electrolytes meet again and react on the electrodes, releasing electrical energy.

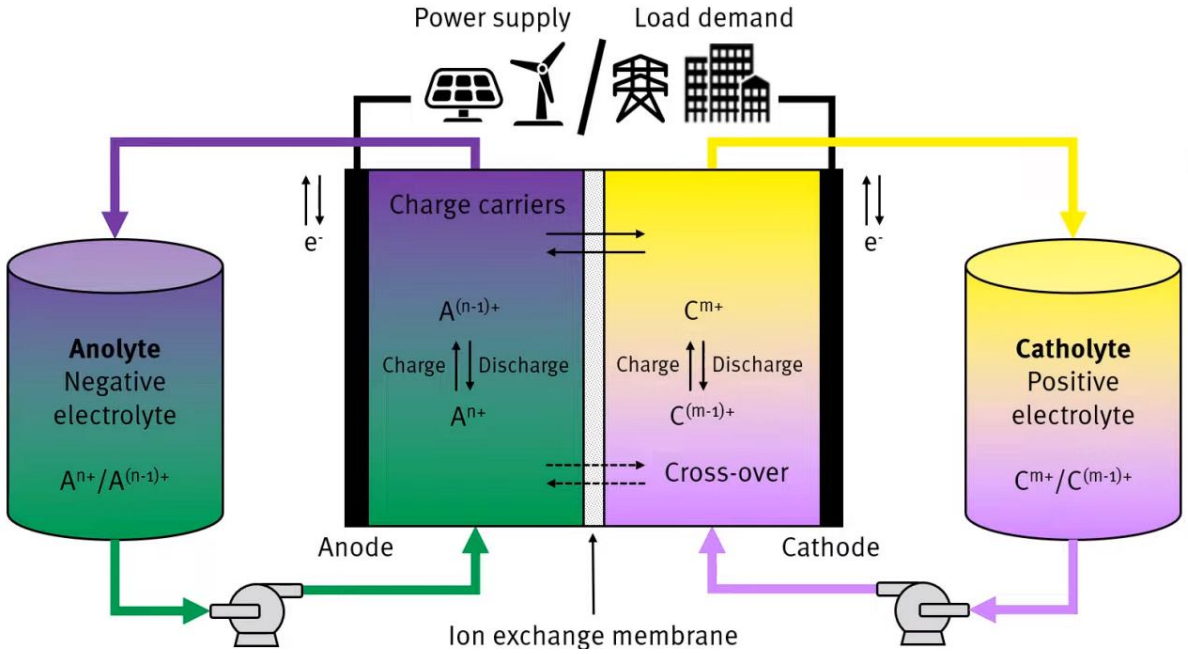


Figure 1. The Component and Mechanism of Flow Battery [4]

Now, when delve deeper into the actual situation inside a liquid flow battery, as shown in fig.2. First, it places the electrolyte in two outer tanks, called negative electrolyte analytes and positive electrolyte capacitors, which store energy. However, it must pump the electrolyte into a liquid flow battery pack with an anode for the analyte compartment and a cathode compartment for the cathode stone in order to add or subtract energy. An iron exchange membrane separates these two liquids, allowing charge carriers to pass between the two electrolytes but restricting the mixing power. The flow battery can then be powered or discharged by altering the electrolyte's state of oxidation. Even though the barrier is made to prevent the mixing of two electrolytes, crossover can nevertheless occur to some extent and reduce capacity.

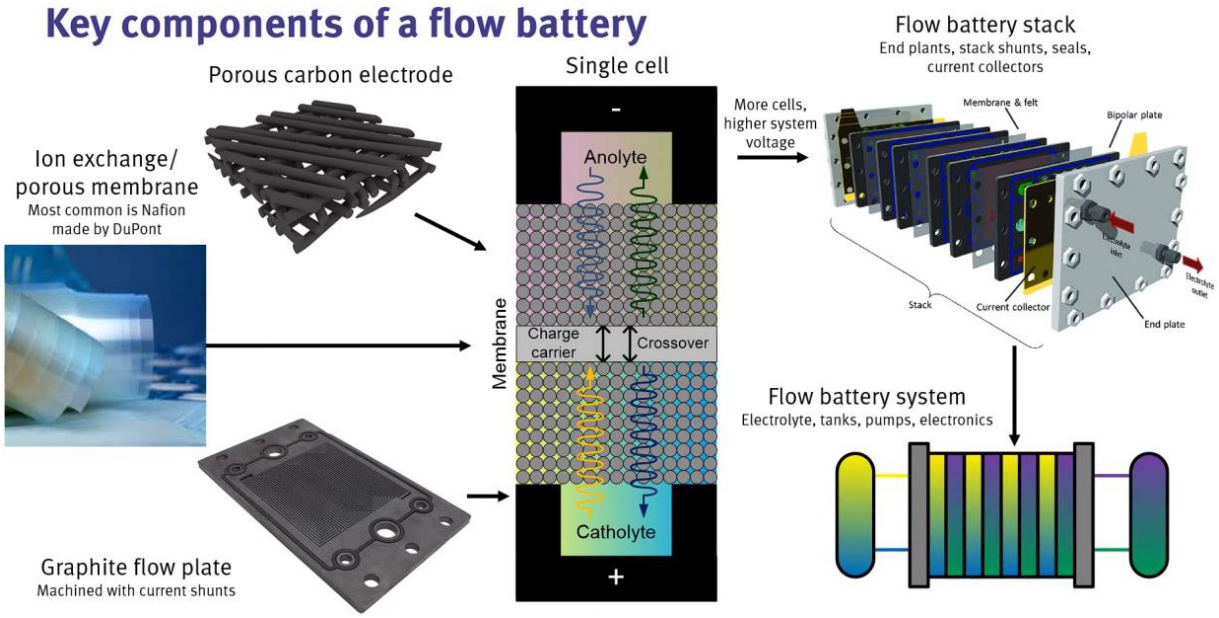


Figure 2. Cross sectional area of flow battery [4]

Although in some systems, various components can be seen on the cross-section of the flow battery, including a porous carbon electrode, on both electrodes, it is usually made of carbon paper or felt,

which provides a pathway for electron conduction but also allows electrolyte penetration and diffusion through the battery. These two porous carbon electrodes are separated by an ion exchange membrane that does not allow electrons or electrolytes to flow through, but now does allow charge carriers to pass through. Although there are several options in many cases, it is made of a material called Nafion, a sulfonated fluoropolymer discovered by DuPont [5]. Then, these components are sandwiched between two graphite plates, which guide the electrolyte to the reaction site on carbon paper. Liquid tight sealing is important for durable systems. At the same time, it can increase the surface area of a single battery to increase the maximum current, and then integrate the liquid flow battery pack into a system with an electrolyte tank pump and electronic devices to control the system.

3. Flow Battery Technology

3.1. Flow Battery Technology

Generally, this can be broken down into 2 main categories depending on the active materials. In one of these we have a liquid or gas electrode paired with metal such as the zinc-bromine system. And then we have the liquid-liquid system such as the all vanadium and iron-chromium systems.

All of which have had some degree of commercialization. Beyond these chemistries there are number of other promising systems which are either under development or at the lab prototype stage all with different pros and cons, however to-date, only the all vanadium and zinc-bromine systems have gained appreciable commercial traction. Now when we're considering a flow battery chemistry, one of the most important aspects is the positive and negative electrolyte. Here the ideal properties are that it should have a good reactivity, for high efficiency and it should have a large stability window for high lifetime and performance. Therefore, in this plot which shows different redox couples we want to pick a pair which have a large difference in voltage and which have high reactivity which is shown by the height of the lines. However, one of the problems is that many of these systems are aqueous, i.e. they use water, and therefore we should be careful that certain redox couples could lead to hydrogen or oxygen formation which leads to poor lifetime. Once we've selected a chemistry, we then need to consider the flow battery components such as membranes and flow fields. These are then stacked together to build up the voltage. And then ultimately integrated into systems with power electronics and control.

3.2. Types of Liquid Flow Batteries

3.2.1. All-vanadium flow battery

The all-vanadium flow battery is currently one of the more commercially developed chemistries among those that are available. The advantage this type of battery is high theoretical lifetimes since crossover effects are not irreversible since vanadium is used on both sides of the battery and thus can be rebalanced. The redox potential of the V^{2+}/V^{3+}anode reactional so mean that there are limited hydrogen side reactions leading to higher stability, and given the relatively high reactivity of the redox couples means that expensive catalysts are not required for effective operation The disadvantages of this systems however include the price volatility of vanadium. Most of which is a product of the steel manufacturing process. And also, the low energy and power density of this system relative to lithium-ion though this is less of an issue for stationary

3.2.2. Zinc bromine flow battery

The next most popular chemical is a zinc-bromine flow battery, which is a little different from an all-vanadium device. Here, a zinc-bromide salt solution that has been dissolved in water is employed as the electrolyte. Bromide is changed into bromine during charging, creating a voltage of 1.08 V at the positive electrode and -0.77 V at the negative electrode thanks to zinc plating. When discharging the battery, the reverse reaction occurs with this redox couple giving a voltage of 184V and given that a deposition reaction occurs atone electrode, we call this a hybrid flow battery [6]. The advantage of this is that the materials are relatively cheap, both in terms of electrolyte and membrane, and the

system has a reasonably high energy density and voltage for a flow battery. meaning that they have found some application in residential energy storage where space can be at a bit more of a premium. The disadvantage of this system relative to a vanadium flow battery is that the lifetime is generally lower since there are crossover issues and safety issues can arise through the formation of zinc dendrites and toxic bromine gas which results in slower charge rates and occasional maintenance cycles.

3.2.3. Iron chromium flow battery

And the final flow battery chemistry is the iron-chromium system. This is much more similar to the earlier all-vanadium system in that liquid electrolyte is used on both sides of the flow battery. On the positive electrode, a liquid electrolyte consisting of Fe^{2+} and Fe^{3+}ions are used with a voltage of 0.77V. And on the negative electrode a liquid electrolyte consisting of Cr^{3+} and Cr^{2+} ions are used with a voltage of -0.41V. Combined this therefore gives a cell voltage of 1.18V. Now the advantage of using this system is that both iron and chromium electrolytes are relatively cheap. However, the disadvantage is that the energy density is low and the kinetic of the chromium reaction are also slow resulting in a large system. Furthermore, the potential of the chromium reaction means hydrogen evolution can readily occur and cross over of dissimilar electrolytes can lead to accelerated and irreversible degradation. Despite these challenges companies such as Ener Vault have attempted to commericalise this technology, though with limited success due to these issues.

4. Advantages and of liquid flow batteries

There is difference of performance of lithium battery and flow battery, as shown in table 1 [7]. Electric vehicle energy storage refers to the battery energy storage system mounted on electric vehicles, which has the ability to store, release and recover electrical energy. The electric vehicle energy storage system includes three parts: battery, motor controller and charger. Among them, the battery is the core part of the electric vehicle energy storage, mainly composed of battery cells, battery management system and cooling system. The technology currently used for electric vehicle energy storage is lithium battery technology, which has the characteristics of high energy density and long cycle life. But lithium batteries also have some disadvantages [8]. One is resource dependence; the second is environmental pollution, because its electrolyte contains a large amount of toxic heavy metals, which will cause great harm to the environment; finally, there are safety hazards. As a new energy storage battery, flow battery has the advantages of high cycle life, high safety and stability, and green environmental protection [9]. If flow batteries can be used for electric vehicle energy storage, it will break through the bottleneck and bring the field into a new height.

Table 1. Performance of differences between lithium battery and flow battery [7]

Battery type	lithium battery	Flow battery
Energy density/ (Wh/kg)	90-190	15-40
Charging efficiency (%)	95	80
Comprehensive utilization efficiency (%)	90	75
Normal temperature cycle life/time	4000	15000
Investment costs/yuan (kW/h)	3000	4000

5. Limitations of Liquid Flow Batteries

From the perspective of development restrictive conditions, the initial investment level of flow batteries is high, and they are at a high level in various types of battery energy storage; The flow battery has a low energy density, lower than that of lead-carbon battery, the volume and weight of the equipment are large, and the electrolyte contains concentrated sulfuric acid (2 ~ 3 mol/L) to improve the solubility of pentavalent vanadium and the oxygen evolution potential of water, which has certain toxicity [10].

6. The Application of Flow Battery

Grid energy storage refers to a group of techniques for extensive grid energy storage. When electricity is cheap and plentiful (especially from intermittent power plants like renewable energy sources like wind, tidal, solar, etc.) or when demand is low, it is stored; however, when demand is high and prices are higher, it is returned to the grid. Grid energy storage system needs to respond very quickly when people need more electricity. There is full of electrolyte in the flow battery which means that flow battery has faster response time.

For the last point, such a huge system cannot be broken easily because the fixing and reestablishment need several months or even for years. Fortunately, the positive and negative active substances of flow battery exist only in the positive and negative electrolytes respectively, which means that it there are no phase changes common to other batteries during charging and discharging. In this case, flow battery has much longer life than other batteries. And currently Canada's longest commercial demonstration of the vanadium battery module has been operating normally for more than 9 years.

The next part that flows battery is good at is the solar energy storage. Solar energy is a very environmentally friendly energy source, but due to the influence of weather and other factors, the efficiency of solar energy is not high. Iron-chromium flow batteries can store solar energy and release it when needed, thereby improving the efficiency of solar energy utilization. In addition, ferrochrome fluid is galvanic. The pool can also supply power to the home at night or on cloudy days, thus achieving all-weather utilization of solar energy.

7. Future Outlook

Liquid flow battery technology is still constantly developing, and researchers are working hard to overcome its limitations. The future development trends include:

New electrolyte materials: Search for cheaper and more efficient electrolyte materials to improve performance and reduce costs.

System integration: Integrate liquid flow batteries with other energy storage technologies to improve the efficiency of the overall energy system.

Commercialization and market expansion: It is expected that with the maturity of technology, liquid flow batteries will occupy a larger share in the electricity market.

8. Conclusion

Liquid flow batteries, as an energy storage technology, have broad application prospects. Although they still face some challenges, with the continuous improvement and commercialization of technology, liquid flow batteries will play an important role in fields such as power systems, renewable energy integration, and industrial applications. Future research and development will continue to promote the progress of liquid flow battery technology, making contributions to clean energy and sustainable development. So, to conclude, there is an undoubted increase in renewables generation which is great, however deployment of these renewables will likely result in issues around power network stability Flow batteries have the potential to be a low cost safer and more durable option than lithium-ion batteries. Some of these advantages come from their ability to decouple power and energy, with the size of stacks representing power and the size of electrolyte tanks representing the energy. Here there are quite a few components in the system making them more complex and requiring scaling. The 3 main flow battery chemistries currently being commercialized include the vanadium, zinc-bromine andiron-chromium flow batteries. Here the all-vanadium system is currently the most widely adopted because of advantages in lifetime however significant improvements are still required and there is lots of room for innovation in emerging chemistries.

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