

Analysis on Flow Battery Ion Exchange Membrane

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Abstract. Flow batteries have emerged in recent years, and ion exchange membrane is the most important component in flow battery. The performance of the membrane determines the service life of the flow battery. This paper reviews the different types membrane such as bipolar membrane, amphoteric IEMs, proton exchange membranes. The application of each type membrane and the method to of synthesizing membrane are discussed. Environmental pollution is also a concern at present, for the production of three different flow batteries (vanadium redox flow battery including zinc-bromine flow battery and all-iron flow battery), this article combined with the environmental impact of all aspects of the analysis. In the end, this paper discusses the technical issues that need to be resolved.

Keywords: flow batteries, ion exchange membrane, bipolar membrane, amphoteric IEMs, proton exchange membranes.

1. Introduction

In recent years, the existing energy resources have been continuously exhausted due to ordinary use, which may lead to a serious global energy crisis, and the problem of environmental pollution caused by use is also concerned. In order to better meet the rising demand for fuel, reduce greenhouse gas emissions, and moderate the rate of global warming, researchers have been trying to discover new and renewable energy sources. By comparing various energy storage technologies, electrochemical energy storage systems have become the best combination of efficiency and cost, and for storing electricity in medium- to large-scale applications, REDOX flow batteries are thought to be the best option. Film is the key component of REDOX flow battery, and its service life determines the performance of the battery. As a separator in the flow battery, the membrane prevents the cross mixing of positive and negative electrolytes and allows ions to complete the transmission of the circuit in the process of current passing, which plays an important role in the battery.

The membrane of REDOX flow battery is an important part of it. Following features are necessary for a perfect membrane including low swell ability, low electrical resistance, low-cost, good chemical stability, permeability resistance, high ionic conductivity and selectivity, also has high chemical, mechanical and thermal properties, as shown in fig.1 [1-4]. The membrane material has a low resistance characteristic, thus reducing the loss of current, which can improve the energy efficiency of the battery. Good chemical stability, can prevent electrolyte adverse reactions. It is high ionic conductivity so that ions between the positive and negative electrodes can transfer charges through the membrane more freely and quickly. Permeability resistance prevents battery performance from decreasing due to electrolyte mixing between the cathode and anode.

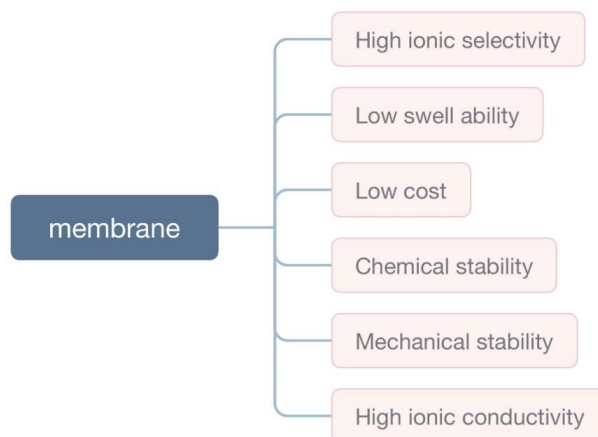


Figure 1. Ideal membrane factor

2. Different Type Of IEM

Ion Exchange Membrane (IEM) is a membrane material used for separating and transporting ions. It has highly selective ion transport properties that allow specific types of ions to pass through while blocking the transport of other ions.

There are lot of different type of IEM can be applicable for flow battery, and they all have their own unique characteristics. These membranes include anion exchange membranes (AEM), cation exchange membranes (CEM), bipolar membranes, amphoteric IEMs, Proton Exchange Membrane (PEM), monovalent selective IEMs, mixed matrix membranes (MMMs) [5]. AEM contains positively charged functional groups that retain cations and allow only anions to pass through. CEMs has negative charged functional groups that reject anions and allow only cations to pass through [6, 7].

The primary elements of the bipolar membrane include the foundational structure, active functional group, and supporting matrix, including anion exchange groups and cation exchange groups [8, 9], which is composed of two layers with a negative cation exchange layer (CEL) and a positive anion exchange layer (AEL) composed of polymer film. No ions are transported between them, and bipolar membranes are mainly used for electrodialysis applications. The electrochemical performance of BPM is determined by the performance of the hydrolytic ionization catalyst placed at the cation/anionic interface and the performance of the unipolar layer [10]. The cation exchange substances of bipolar membranes basically contain sulfonic acid group, and a few contain phosphoric acid group [11].

Amphoteric IEMs also contain both cation exchange groups and anion exchange groups, but they are not stay together. The efficiency and durability of a battery can be directly impacted by the Anode Interface Electrochemical Migration (AIEM) [12]. The AIEM can improve the performance by regulating the structure of the polymer so that VRB become batter. Similarly, to guarantee the effectiveness of the membrane, it is essential to consider the significance of both the reduced permeability of vanadium ions and the enhanced proton conductivity [13].

Proton exchange membranes are usually made of polymers containing proton exchange groups. PEM can play a key role in aquatic hydrogen electrolysis. PEM has good proton selectivity, high chemical stability and good temperature adaptability. Proton selectivity makes PEM virtually non-conductive to electrons, while high temperature adaptability allows PEM to continue efficient proton conduction at lower or higher temperatures.

3. Different Type of Membrane Applications

3.1. Bipolar Membranes

The primary technique utilizing bipolar membranes is known as bipolar membrane electrodialysis (BMED). This process can be used in many fields. They are mainly used for resource regeneration

and recycling, capture of carbon dioxide and sulfur dioxide, waste water and sludge treatment, auxiliary energy source, and food industry [8]. In resource generation and recycling, BMED can produce acids and bases from salt solutions. Similarly, it can be used in industry as a step to recover acids and bases. However, BPM and BMED are very expensive, so they are still rarely used in the market. The BMED process is also utilized in the synthesis and reclamation of organic acids. But, due to the immaturity of the technology, it has not been widely used. BMED can produce ammonia from wastewaters or fermentation mixtures [14, 15]. In the field of capture of CO₂ and SO₂, BPM for capturing CO₂ from water and atmosphere can make a significant contribution to the environment [16, 17]. Carbon dioxide can be fed into the battery for reduction as a gas stream [18, 19] or as dissolved CO₃²⁻ and HCO₃⁻ ion in aqueous solutions [20, 21].

BPMs can be used to capture SO₂. Its principle is to desulfurize the air flow and then feed it into the bmed device to obtain an alkaline solution [22]. SO₂ can be recovered by reducing pressure, heating and inert gas sparging [8].

BMED can be employed for the elimination of ionic pollutants [23] and recover compounds from wastewater streams. The BMED process can inhibit the precipitation of chlorine gas, which has obvious advantages compared with simple electrochemical cells with only CEM. Also, other application of BMED is that they can be utilized for the retrieval of heavy metals and essential raw materials [8]. For example, BMED can be used to remove copper and nickel from municipal sludge [24].

The BPM can serve as an acid-alkali flow cell because it has the ability to store electricity by reversible pH and salinity gradients [25]. Because of these characteristics, its energy density can be more than three times higher than that of other batteries. Similarly, bipolar membranes can be employed to sustain both acidic and alkaline environments within the electrode chamber of a solar fuel cell [26, 27].

In the food industry, BMED can be employed for the extraction and reclamation of organic acids from fermentation broths [28, 29], as well as the retrieval of volatile fatty acids (VFAs) from pig manure [30]. In some practical applications, bpm can be used to extract or separate fats and proteins from dairy by-products [31, 32] to convert polysaccharides to oligosaccharides [33], and to extend the shelf life of foods using acidifiers [34].

3.2. Amphoteric Ion Exchange Membrane

Amphoteric ion exchange membrane (AIEM), as the important part of Vanadium redox flow battery (VRB). The VRBs constituted by AIEM can be wide application in power supply system [35], power source of electric vehicles, providing an interruptible and emergency power supply [36,37]. VRB is used in the energy storage system of electric vehicle charging stations, which can quickly release power to charge electric vehicles when there is a lack of power. Similarly, the gases emitted do not pollute the atmosphere. VRB as emergency power supply, it can provide electricity for public places in time When electricity is scarce [38].

3.3. Proton Exchange Membranes

The main applications of proton exchange membranes are fuel cells, water electrolysis equipment and fuel cell vehicles. In fuel cell applications, PEM conducts protons from hydrogen molecules to the cathode side where they react with oxygen to produce water, releasing electrons to drive external circuits. Water electrolysis equipment can use the proton exchange membrane to transfer the protons generated by the current from the anode to the cathode, which causes the water molecules to undergo a hydrolysis reaction and produce hydrogen and oxygen efficiently. PEM is used as an energy conversion and storage device in fuel cell vehicles, allowing the vehicle to operate with zero emissions and no noise.

4. Synthetic Approach

4.1. Synthesis Of Bipolar Membranes

First, the polymer film is cut into the required size and shape to ensure that the surface of the film is smooth, and then the anode material and the cathode material are coated on one side of the polymer film, so that the anode material and the cathode material are well adhered to the film. Next, the polymer film coated with anode and cathode materials is placed in the oven for drying, allowing the coating to completely dry and cure. Finally, the membrane is cut to a suitable size and the bipolar membrane is assembled.

4.2. Synthesis of Amphoteric Ion Exchange Membrane

There are many different methods to synthesize AIEM and the primary methods utilized include covalent grafting, non-covalent hybridization, and multicomponent copolymerization [39]. Introducing hydrophilic ions through covalent grafting or creating microphase separation structures can lead to high ionic conductivity. High chemical stability and mechanical properties mainly depend on the selection of inert frameworks or the introduction of hydrophobic ions. Irradiation grafting, as a new technology, results in better chemical stability of the synthesized membrane. However, the process of preparing AIEM through radiation grafting method was complex and expensive, necessitating the availability of a radiation source.

Non-covalent hybridization can also improve the performance of AIEM. In non-covalent hybridization, molecules of two or more compounds interact to form a stable complex [39]. First, it is necessary to select a suitable AIE active compound. These compounds typically have rigid molecular structures and large conjugated systems that facilitate the formation of aggregates. These compounds are then dissolved in a suitable solvent and brought together by an appropriate method, such as agitation or ultrasonic treatment. During aggregation, non-covalent interactions occur between compounds to form stable complexes. Finally, the complex is separated or purified from the solvent to obtain pure non-covalent hybrid AIEM.

Among these three methods, multicomponent copolymerization is the simplest and also the lowest cost. First choose the appropriate monomer, and determine the proportion of monomers, you can consider the use of different monomer combinations to obtain a diversity of polymers. According to the characteristics of selected monomer and reaction system, the reaction temperature, time and solvent selection are optimized. Secondly, the selected monomer is added to the reaction vessel according to the formula, and the appropriate initiator or catalyst is added to carry out the copolymerization reaction. Finally, the copolymer was separated from the reaction system and purified to obtain pure multi-copolymer AIEM.

4.3. Synthesis of Proton Exchange Membrane

Fluorinated polymers and non-fluorinated polymers can be used in synthesis of PEM. Fluorocarbon-based ion-exchange membranes with good chemical and thermal stability. The film prepared by this method has good electrochemistry and durability in harsh environment, but it is difficult to make and the cost is high.

Hydrocarbon-based polymers are composed of polar groups and high-water carbon mainchains that increase the proton conductivity in the membrane [40]. Incorporating rigid sites within the polymer framework can enhance the stability and functionality of the membrane.

5. Environmental Impact of Production Flow Batteries

As an energy storage system, flow battery is a long-term renewable resource available. The main goal of grow used to the renewable energy is to reduce the impact on the environment, but the production of energy storage systems and the use of technology also have an impact on the

environment. Therefore, in order to better reduce the harm to the environment, it is crucial to comprehend the influence of energy storage systems on production.

Vanadium redox flow battery (VRFB), zinc-bromine flow battery (ZBFB) and all-iron flow battery (IFB) as the most commonly used flow battery cells, their production will have a certain impact on the environment. The following will mainly from Global warming potential (GWP), Ozone depletion potential (ODP), Fine particulate matter (PM), Acidification potential (AP), Fresh water eutrophication (EP), Cumulative energy demand-fossil fuel (CED), Freshwater ecotoxicity (ETP), Abiotic Resource Depletion (ADP) these aspects to compare their impact on the environment [41].

In the production of VRFB, impact on GWP, ODP, PM, AP, EP and CED are all greater than ZBFB and IFB. In the effect of producing VRFB on GWP, PM, A and PCED, the ES electrolyte is all occupy the most part. It can produce more than 120 kgCO₂ eq/kWh in GWP, 4700 MJ/kWh in CED, 0.21 kg PM_{2.5} eq/kWh in PM and more than 0.6 kg SO₂ eq/kWh in AP. The one occupying the least part is the BOP accessories. In the effect of ODP, production of ES occupies the largest part, it more than 0.000013 kg CFC-11 eq/kWh in ODP. In the effect of EP production of CS cell frame, it uses more than 0.04 kg P eq/kWh in EP, and uses for production BOP power conditioning system. ES electrode and BOP battery management system impact on EP is basically the same [41].

In the environmental impact of producing ZBFB, in terms of the impact on GWP, PM, AP, EP and CED, ZBFB is lower than VRFB and higher than IFB. In the production component of CS biopolarplate are all take up the largest proportion in these potential environment impact. For production component of CS biopolarplate it uses more than 60 kgCO₂ eq/kWh in GWP, more than 0.000012 kg CFC-11 eq/kWh in ODP, 0.15 kg PM_{2.5} eq/kWh in PM, 0.25 kg SO₂ eq/kWh in AP, 0.03 kg P eq/kWh in EP and 8000 MJ/kWh in CED. Production component of ES electrolyte has significant impact in ADP which is large than 0.035 kg Sb eq/kWh, and also ZBFB in these kinds of impact for environment is the largest compare with other two type of flow batteries. In production component for ZBFB is the least impact in ETP of the three flow batteries [41].

In the environmental impact of producing IFB. In addition to the ODP and ETP effects, the other environmental impacts are the least of the three flow batteries. Production component of CS membrane for IFB is more than 0.00007 kg CFC-11 eq/kWh in ODP. Production component of CS biopolar plate and CS membrane take up the two biggest proportion in ETP. For impact on ETP CS biopolar plate uses 0.35 PAF·m³·day/kWh, CS membrane uses 0.5 PAF·m³·day/kWh [41].

6. Technical Issues that Need to be Resolved

Vanadium REDOX flow batteries (VRFBs) are used today in a variety of stationary applications. VRFB has the strength of flexibility, long shelf life, high efficiency, but the same high cost of use, electrolyte imbalance affecting the battery capacity has become the main problems facing VRFB, these problems make the market very few VRFB system. In order to optimize the use of VRFB, some technical improvements are needed to solve these problems.

In the long-term operation process, the concentration of cationic ions is not balanced, and the concentration of cationic ions in the electrolyte is not balanced, which will lead to the electrolyte imbalance. If the concentration of one of the ions is too high or too low, it will cause an imbalance in the electrolyte. Similarly, if the electrolyte flow is not uniform, the electrolyte in some areas may be over-consumed, resulting in electrolyte imbalance. The electrolyte is blocked by the membrane, and the pollution or damage of the membrane will make the electrolyte mix, and then cause the electrolyte imbalance. To avoid the above situation, you can adjust the concentration of cations and anions in the electrolyte formula, regularly check the integrity of the film, and replace the film in time. When the flow is found to be uneven, measures such as adjusting the flow speed or adding nozzles are used to ensure that the electrolyte flows uniformly in the battery, so that the electrolyte reaches a balanced state.

The primary factors contributing to the high expenses of VRFB are the cost of vanadium, the cost of membrane materials, and the cost of system construction. Vanadium as a rare metal, the price is

relatively high, the ion exchange membrane is used to separate the anode and cathode in VRFB, the price of high-performance ion exchange membrane materials is also very expensive, the same equipment and facility construction also requires a high cost. With the development of technology, the cost of VRFB may decrease in the future.

7. Conclusion

With the development of flow battery technology in recent years, the research of ion exchange membrane has also attracted much attention. In order to make the synthetic ion exchange membrane close to the ideal membrane state, the synthesis technology of the membrane is still improving year by year. The environmental impact of the synthetic membrane technology needs to be overcome, and this impact will be reduced as future synthetic technology improves. Future investigations on membranes will primarily focus on the exploration of inexpensive materials, as well as the advancement of ion exchange membranes possessing high ion conductivity, selectivity, stability, and durability.

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