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Performance Comparison of Sulfonated Polyimide/PTFE-Reinforced Membranes for ZnBr Flow Batteries

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Abstract. Zinc Bromine Flow Battery (ZBB) is an energy storage system that can be applied as a storage for renewable energy. The core material of ZBB is a membrane. The required characteristics of the membrane were low electric resistance, high ion conductivity, and excellent bromine resistance. For the purpose, two different type membranes are used to 6cm^2 ZBB cell operations: one is PTFE#1 (porous PTFE membrane) based on a nafion with silica and the other is PTFE#2 (hydrophilic PTFE membrane) based on an aquivion with hollow silica. The performance comparisons are carried out using 2.0M $ZnBr_2$ solution and OCV comparisons are carried out using 1.0M $ZnBr_2$ solution. According to the experimental results, it is considered that both types of membranes can be used in ZBB since they are normally charged and discharged. Also, it was confirmed that the bromine permeability was lower than that of SF600, which was commercialized.

Keywords: Energy storage system, Zinc bromine redox flow battery, PTFE membrane.

1. Introduction

As a countermeasure for solving the environmental problems caused by the use of fossil fuels, research and dissemination of renewable energy generation systems such as solar power and wind power are being actively carried out all over the world. However, it is difficult to secure the safety of electric power supply because renewable energy such as solar and wind depends on highly volatile natural energy. Therefore, large-capacity power storage technology is needed to accommodate the volatility of renewable energy, and to smoothly supply electric power and utilize power generation facilities efficiently [1].

Large-capacity power storage technologies can be divided into mechanical, electrical, and electrochemical methods. Of these, electrochemical methods include lead acid batteries, lithium ion batteries, sodium-sulfur batteries, and redox flow battery technology [2]. A redox flow cell is a cell that charges and discharges by reacting two chemical species redox couples having different oxidation numbers in aqueous solution. A number of chemical species have been studied in redox couples for redox flow batteries, and representative chemical species that have been demonstrated or commercialized.

Fig. 1 represents the concept of ZBB. The charge / discharge reaction of ZBRFB is shown in Fig. 1, bromine ion ($2Br^-$) is converted into Br_2 at the anode and zinc ion (Zn^{2+}) is converted into zinc (Zn) at the cathode at the time of charging [3]. In the Zn-Br redox flow cell, Zn precipitates at the anode during charging, and the bromine anion moves through the membrane and reacts with the deposited Zn to self-discharge with $ZnBr_2$, which results in a decrease in efficiency. In this study, the characteristics of the battery according to membrane type were evaluated using two types of PTFE membranes for ZBB. The characteristics of the battery were evaluated by conducting the charging and discharging of ZBRFB using each membrane and evaluating the self-discharge through OCV.

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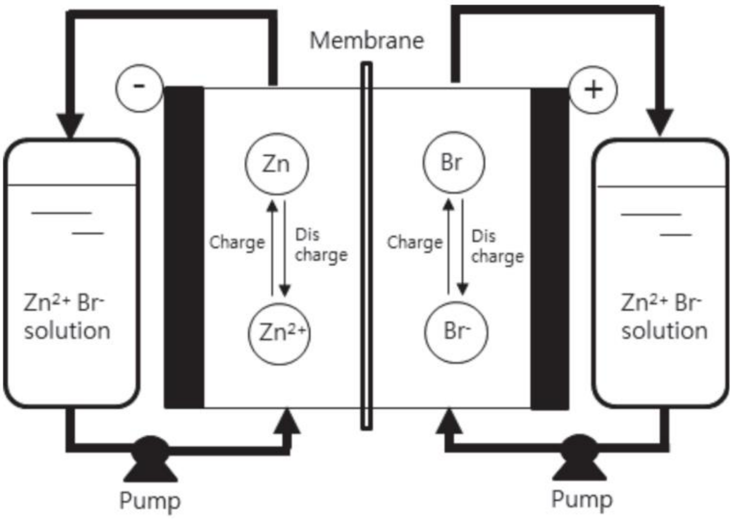

Fig. 1: Concept of the Zinc Bromine flow battery (ZBB).

2. Experimental

2.1. Experimental Preparation

For membrane performance comparison, as shown in Fig.2, 6cm^2 ZBB cell is applied in this work, which consists of carbon felt (Toyobo, 4mm), bipolar plate (SGL, 0.6mm) and membrane. Then, the carbon felt is not used in a zinc-half cell where metallic zinc is plated on the electrode surface during charge [4], [5]. For the experimental preparation, PTFE membranes are treated in the distilled water. PTFE#1 is a membrane impregnated by mixing silica with a nafion in porous PTFE. And PTFE#2 is a membrane of ABA type which is a PTFE reinforced layer coated with a composite layer of hollow silica and aquivion.

The cell operation is carried out on 50 cycles and the current density is kept constant at 10mA/cm^2. Charge-discharge cycling operation is performed by WBCS3000 (Won-A tech. Korea) with constant charge time at room temperature [6].

2.2. Open Circuit Voltage

Different ionic species tend to diffuse across the membrane because of their concentration gradient across the cell, resulting in coulombic efficiency loss as well as self-discharge. Thus, the ion selectivity of the membrane is one of important parameters that affect the performance of a ZBB. Open circuit voltage (OCV) measurements can be employed as an indirect method to compare the ion selectivity and permeability of various membranes [7]. OCV was charged to 25% SOC using a 6cm^2 cell and voltage was measured to 1V.

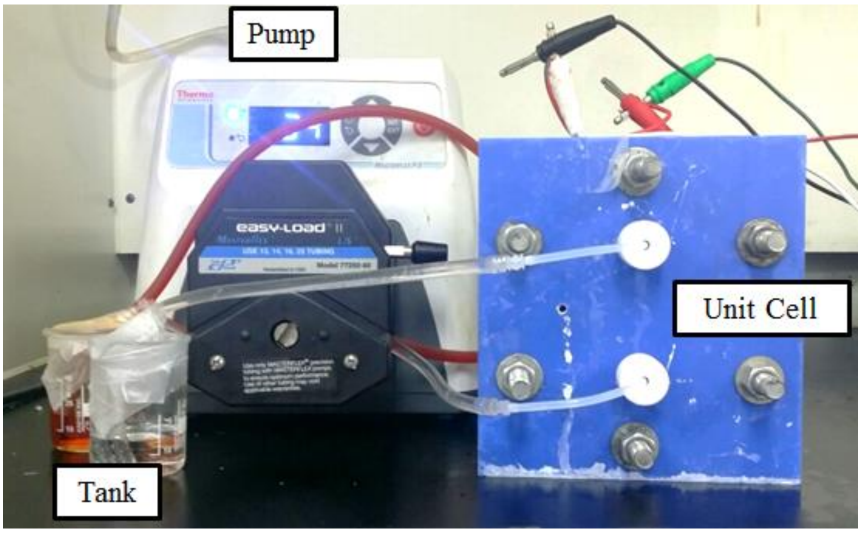

Fig. 2: ZBB cell experiment (active area: 6cm^2, current density: 10mA/cm^2).

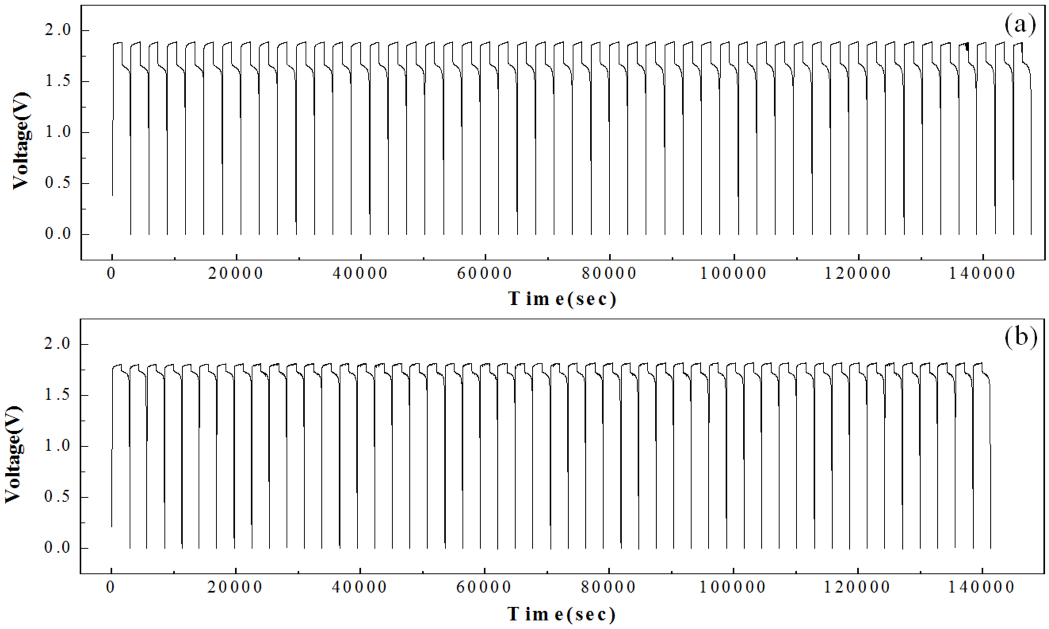

Fig. 3: Cyclic operations due to using (a) PTFE#1 and (b) PTFE#2.

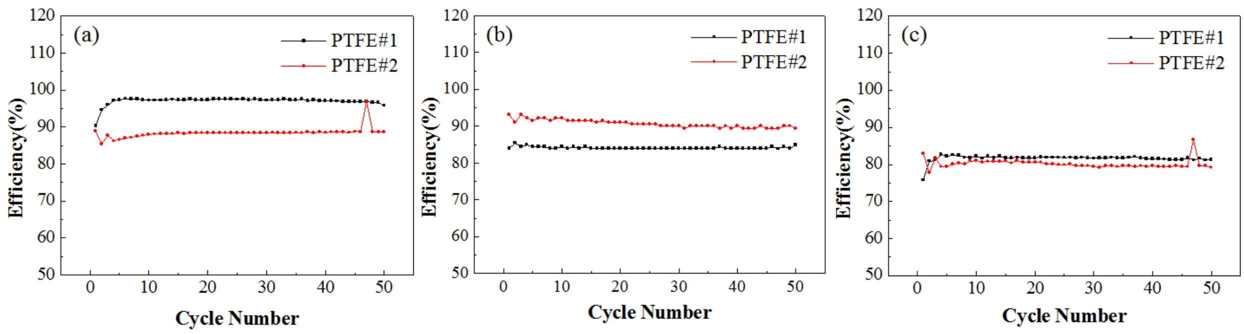

Fig. 4: (a) Coulombic, (b) Voltaic, (c) Energy Efficiency curves due to the cyclic operation of the ZBB cell.

3. Results and Discussion

3.1. Evaluation through ZBB Efficiency

In order to compare the operating performance, Fig. 3 show the charge-discharge curves of the cells using the PTFE#1 and PTFE#2, respectively. Both types of membranes were charged and discharged stably for 50 cycles. It can be seen that the PTFE#1 provides longer discharge times (i.e., higher current efficiency) than the PTFE#2. The performance comparison related to Fig. 4. PTFE#1 shows a higher coulombic efficiency and stability than PTFE#2, but a lower voltaic efficiency. As a result, the energy efficiency of the two membranes was similar.

The thickness of PTFE#1 is 50 ㎛, and the thickness of PTFE#2 is 84 ㎛, which is the average of the four portions of the membrane. Since PTFE#2 is thicker than PTFE#1, the voltaic efficiency should be low, but the conductivity can be improved by using hollow silica. And in order to lower the cost of the membrane, a low cost aquivion was used in PTFE#2 instead of the expensive nafion used in PTFE#1. It is considered that the ion resin change did not affect the performance.

3.2. Evaluation of Br Permeability through OCV

Fig.5 is an OCV graph using three kinds of membranes. SF600 is porous separator based on a hydrocarbon that the most widely commercialized in the ZBB market. However, it only shows good efficiency when using a complex agent for Br stability [8]. In this experiment, the cell was operated using an electrolyte without a complex agent. PTFE # 2 is thicker than PTFE # 1, but as hollow silica is used, it has been confirmed that Br movement is more active and self-discharge is faster. In addition, SF600 is a porous separator, and it can be seen that self-discharge is faster than PTFE # 1 or 2, which is a cation separator.

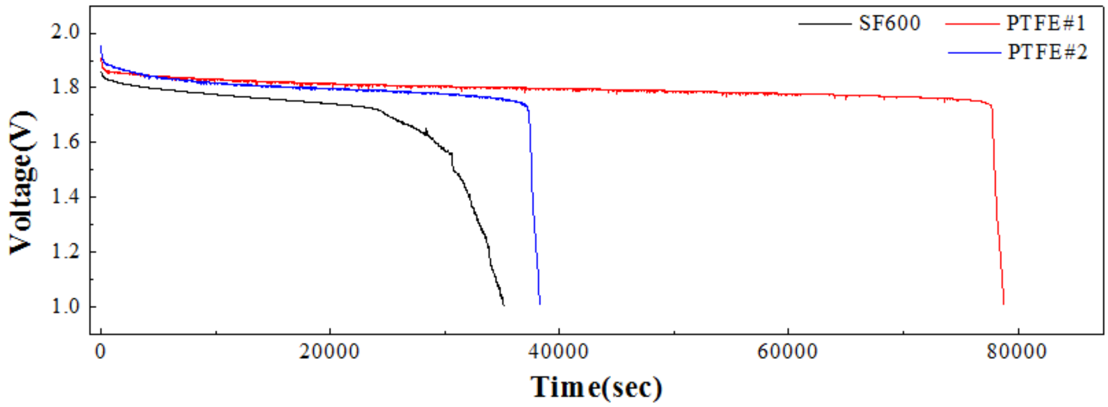

Fig. 5: Discharge curves due to open circuit voltage of the ZBB cell.

4. Conclusion

In this paper, two types of membranes fabricated using PTFE were compared and evaluated. Both PTFE # 1 and PTFE # 2 appear to be available in ZBB. The two types differed in terms of coulombic efficiency and voltaic efficiency. In case of PTFE#1, the crossover of Br was lower than PTFE#2 and the coulombic efficiency was higher, but the voltaic efficiency was lower due to the use of general silica. On the other hand, PTFE#2 showed higher voltaic efficiency by using hollow silica, but the coulombic efficiency was lower because of self-discharge. According to these results, it was confirmed that a fluorine-based cation separator using PVDF can be used for ZBB. Therefore, it is considered that it is possible to fabricate a PVDF membrane capable of improving the performance of ZBB by controlling the hollow size and addition amount of silica.

5. Acknowledgements

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6. References

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