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Preparation and characterization of new stack of zinc-bromine redox flow battery based on nafion/PTFE composite membrane

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ABSTRACT

A new Zinc-bromine flow battery stack consists of graphite bipolar plates and based on Nafion/PTFE composite membrane. Our battery stack is made up of three single batteries. The electrochemical behavior of the stack are investigated and discussed in terms of charge-discharge property, energy storage capability and cycle life. Good charge and discharge capacity could be obtained during the first cycle and the discharge efficiency reaches up to 75%. The energy yield remains almost constant during a fairly large number of cycles.

KEYWORDS

Zinc bromide battery;
Charge-discharge;
Energy storage.

INTRODUCTION

The zinc-bromine redox flow battery, an electrochemical system that store energy in the solution, should be considered as to be highly attractive for energy storage. The zinc-bromine battery is constituted of tanks that supply the reaction cell with the cathodic liquid (catholyte) and anodic liquid (anolyte). In the process of charging, zinc deposits on the surface of negative electrode[1,2], and bromine stores in the bottom of the anode tank with oily complex formation[3,4]. The electrical potential difference of redox electrode pair is the driving force to react. Zinc- bromide cell power depends on the area of plate electrode within the single battery and the number of section. Energy storage capacity depends on the tank capacity of reservoir and electrolyte concentration. So cell power and energy storage capacity can be designed separately, which is suitable for large capacity storage of electricity.

Zinc bromine battery have many advantages, especially in cost[5], because the cost of electrolyte, to a great degree, determines the overall cost of the battery. It's estimated every KWH cost of Sodium sulfur battery and vanadium battery is about $500, however, the cost of zinc bromine battery is only $100 or so. This is equal to the price of common lead-acid battery. Compared with lead acid battery, zinc bromine battery is of high energy density and power density, as well as good charge and discharge properties. Besides, zinc bromine battery works at normal temperature, rather than working with sophisticated thermal control system.

Until now, in spite of many experiments have been put into effect, there are still a few technical problems unsolved. The problems are principally related to bromine diffusion towards the zinc electrode, but also to zinc dendrite formation, could not be completely worked out so far. To improve cycle lifetime and reliability of the system, many technical solutions have been put forward, such as the use of Br_2 complex agents to keep bromine diffusion in the aqueous phase[6,7]. The development of bipolar plate notably improves the quality of zinc plating. Although high self-discharge rates and poor cycling capability still hinder the industrial development of Zinc-bromide cells, these problems are outside the scope of this work.

At present, the key materials for Zinc-bromide redox flow battery, for example, bipolar plate materials have been becoming the emphasis of the research. Three types of bipolar plate materials are graphite, metal and carbon-plastic. Among them, graphite has good conductivity, heat conduction performance, stable chemical properties, corrosion resistance and low thermal expansion coefficient. Therefore, graphite is the first to be applied in the production of bipolar plate. But there are some certain disadvantages such as brittle and mechanical strength low[8-10], needing to graphitization processing[11-12]. The graphite bipolar plates in this paper are made to order according to our needs, whose resistivity is low.

In this paper, we used a thin Nafion/PTFE composite membrane for zinc-bromine redox flow battery stack, which, to our knowledge, has not been reported previously. Nafion/PTFE composite membrane[13-16] provide good mechanical strength and low cost. The aim of this work was to assemble a zinc- bromine flow battery stack and evaluate the properties of its charging and discharging, but also to investigate AC impedance of the stack.

EXPERIMENTAL

Preparation of nafion/PTFE composite membrane

The preparation of Nafion/PTFE composite membrane was treated using the method developed by Li et al.[17]. The Nafion/PTFE composite membranes were prepared by exposing porous PTFE film (10ìm thick) extended over a flat glass plate to 5% Nafion (DuPont) solution in 1-methyl-2-pyrrolidinone (NMP)and alcohol. The glass plate was first dried at 70°C, and then dried in a vacuum oven at 120°C for 24 h. The thickness of the composite membrane was controlled by the amount of Nafion solution. The membrane made by ourselves, is thick enough to avoid any short circuit between the electrodes, but also to stop the diffusion of bromine.

Preparations of graphite bipolar plates

According to the design drawing (figure 1), we customized the graphite plates with manufacturers to meet our specific needs. Graphite plate size is 260*160*18. There is a slot on both sides of the plate, and the depth of the slot is 5 mm. On the bottom of the slot, there leaves an S type groove. The advantages of such a design are as follows:

Figure 1 : The designing of graphite bipolar plate

First, the construction is simple. Graphite bipolar plates are used directly as framework components, rather than polyolefin plastic. Every two batteries can align linked to form a series stack. Second, Graphite plates serve as electrodes as well. And the contact area between electrode and solution becomes larger. This leads to efficient charge transfer properties and contributes to Zinc depositing uniformly. What's more, in order to make solution circulate smoothly, there leaves the groove.

Main functions of flow cell bipolar plates are to separate solution and to guide solution into the cell through the flow passageway; in addition, bipolar plate can collect and conduct current. What's more, they take on supporting membrane electrode and heat dissipation.

Development of battery stack

The cell used for this study has been designed as shown in figure 2. The cathode was made of a bulk zinc, and there was a piece of carbon felt in between zinc and graphite plate. Such a design, on one hand, can prevent the zinc moving; on the other hand, can provide good electric conduction during the charge-discharge cycles. When charging, zinc generated would deposit in the cathode zinc and carbon felt, while bromine would flow between anodes and stored at the bottom of the reservoir.

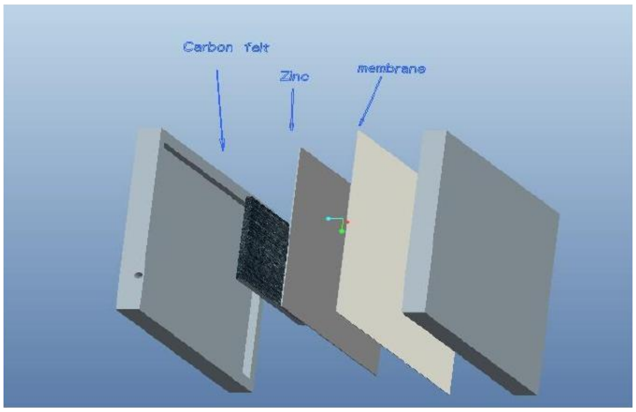

Figure 2 : Component of a cell

There were three single cells made up the stack. The parameters of the stack have shown in TABLE1. It's studied; the highest conductivity is achieved for the molarity of zinc bromide solution close to 2molL^{-1}. The other way, the lowest value of bromine solubility is obtained for zinc bromide molarity about 7molL^{-1}[18-19]. We must keep the conductivity as high as possible, and simultaneously decrease the bromine concentrations in the electrolyte in order to reduce corrosion rates of the cathodic zinc electrode[20]. Therefore, we choose to adjust the molarity close to 4molL^{-1}, because it amount to nearly half of the optimal value not only for the conductivity but for the bromine solubility[21].

TABLE 1 : Parameters of the tested stack

length*wide*high/mm	volume/mm^3	mass/kg	Nominal voltage/V
260*160*70	2912000	2.170	5.4

The anode and cathode electrodes were filled with electrolyte by constant pump. Keep in mind that perfusion should start from the bottom, in order to get rid of air completely. When the top of the electrodes begin to outflow solution stably, the stack was filled with solution. As the constant flow pump driving, the whole pile starts solution circuit.

Electrochemical performance measurement

In our work, battery charging and discharging test was carried through battery testing system 7.5.X. The charge was conducted by a designated current while the discharge was at a constant current. The electrochemical experiments related to the research of the charge-discharge cell behavior have been performed with an electrochemical analyzer CHI604D.

RESULTS AND DISCUSSION

Conductivity measurement

Conductivity measurement was measured using a four-point probe and frequency response electrochemical analyzer CHI604D (Shanghai Chenhua instrument co., LTD). AC impedance measurements were carried out at frequencies between 1 and 10 kHz. AC impedance diagram includes frequency, real part and imaginary part. The real parts of impedance serve as the horizontal axis and the imaginary parts serve as the vertical axis, namely Z=Z'+jZ''. The AC impedance curve is as figure 3. Internal resistance of the stack is about 3Ω.

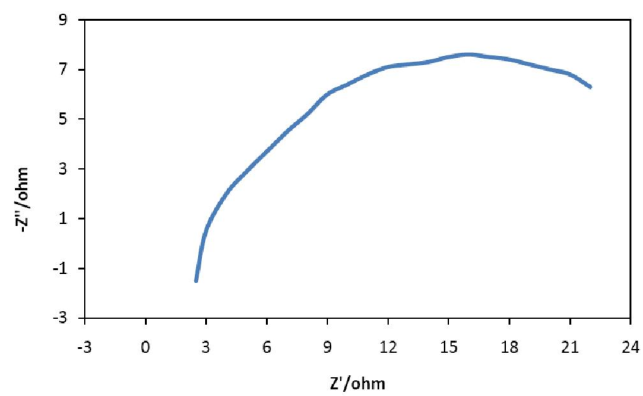

Figure 3 : Conductivity measurement. High freq (Hz) =1e+5, low freq (Hz) =1, amplitude (V) =0.005.

Cell charge-discharge testing

In the first cycle, charge test was carried out using 5A current. Voltage was increasing slowly to 8.6235V. The charging process was for 20 minutes. The current for the discharge progress has been always using 2A for 1 hour. The voltage decreased slowly from 8.6238V. The first charge-discharge curves of the stack are as figure 4 and figure 5. It is found from figure 4 that the voltage goes up on charging and it gets gently at the end of charge. But at the beginning, the voltage falls rapidly for a while, we think this is due to internal short circuits which have developed in the stack. When discharging with constant current, the voltage declines slowly. 11 minutes later, the voltage gets down quickly to 2.1205V, and then goes gently. 30 minutes after discharging, the voltage is almost unchanged for 0.0558V, and the current starts to going down. The discharge progress lasted about 40 minutes.

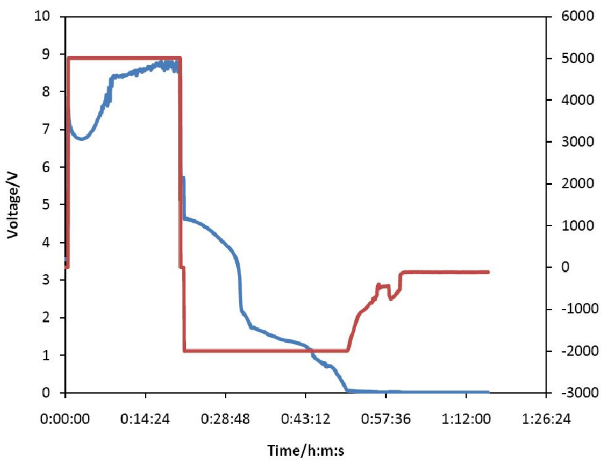

Figure 4 : The first charge-discharge curves

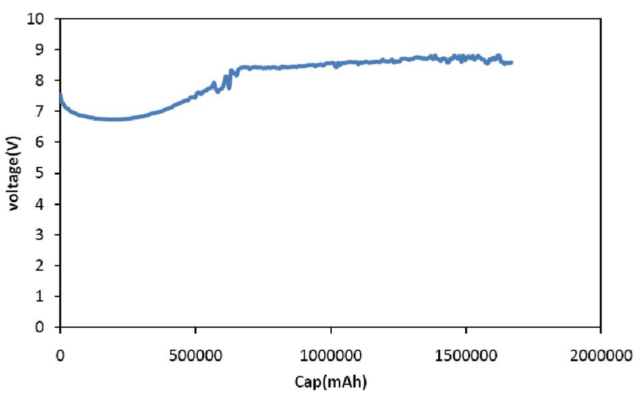

Figure 5 : Charge voltage vs. capacity

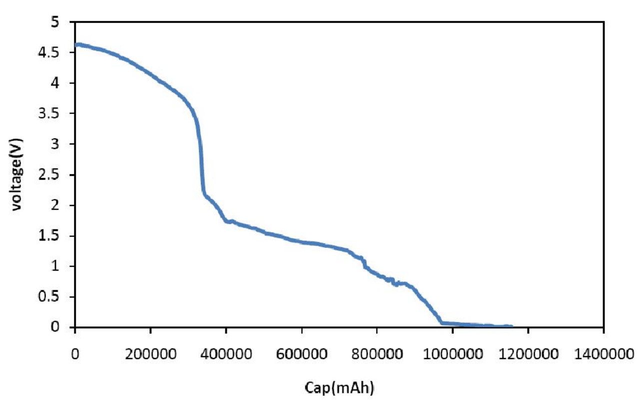

Figure 6 : Discharge voltage vs. capacity

As we can see from figure 5 and figure 6, charging capacity was 1666.7mAh, discharge capacity was 1255.4mAh. And the discharge efficiency reaches up to 75%.

Cycle performance

Cycling is being conducted at 5A charge and 2A discharge. The cycling currents were determined by a consideration of several potential utility applications. After 15 cycles, the open-circuit voltage versus cycle number is shown for good- and bad-performing cases in figure 7. The open-circuit voltage is smooth and steady. Energy efficiency is more than 80% in the later cycles.

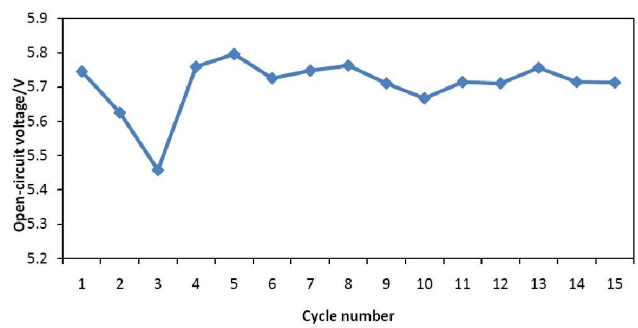

Figure 7 : Open-circuit voltage vs. cycle number

CONCLUSIONS

Our Zn-bromine battery stack has good charge-discharge performance and the recoverable energy yield remains almost constant during a fairly large number of cycles. The discharge efficiency can reach 75%. Besides the energy density and current densities higher than Zn-MnO_2, Ni-Cd, Li-ion and many other commonly used lead batteries. The initial results indicate that the new membrane is a promising material fit for zinc-bromine redox flow battery. The battery stack with this membrane has good performance and provide a path for zinc bromide battery commercial.

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