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An antisymmetric cell structure for high-performance zinc bromine flow battery

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Abstract. Zinc-bromine flow batteries (ZBBs) remain a problem of designing a cell with high coulombic efficiency and stability. This problem is caused intrinsically by different phase transition in each side of the half-cells during charge-discharge process. This paper describes a ZBB with an antisymmetric cell structure, which uses anode and cathode with different surface morphologies, for high-discharge capacity and reliability. The structure of the antisymmetric ZBB cell contains a carbon-surface electrode and a carbon-volume electrode in zinc and bromine half cells, respectively. To demonstrate the effectiveness of this proposed ZBB cell structure, Cyclic Voltammetry measurement is performed on a graphite foil and a carbon felt which are used as the surface and electrodes. Charge and discharge cyclic operations are also carried out with symmetric and antisymmetric ZBB cells combined with the two electrode types. Experimental results show that the arrangement of antisymmetric cell structure in ZBB provides a solution to the high performance and durability.

1. Introduction

Zinc-Bromine flow Battery (ZBB) provide advantages of having cost effectiveness, high energy density, high cell voltage, high long cycle life, low cost of maintenance, for energy storage system [1, 2, 3]. The ZBB electrolyte (composed of an aqueous zinc-bromide salt dissolved in distilled water) is stored in two tanks and circulated through the cell stacks constantly. During charge operation, the zinc bromide salt is divided to zinc ions and bromide ions. Bromide ions which have a low reaction rate [4] convert into bromine molecules and zinc ion deposited on electrode surface as little as reacted bromide ions. On discharge operation, the zinc plated on the negative electrode dissolves in to the electrolyte. But, it can't totally dissolve caused by bromine, which has a low reaction rate. For this reason, low coulombic efficiency is presented. Some researchers had effort for enhancing coulombic efficiency using volume electrode [5]. Also, bromine has a big problem which is high electrochemical corrosion with electrode. For this reason, carbon coated electrode used for enhancing electrochemical resistance with bromine [6]. To whom any correspondence should be addressed.

This paper describes a antisymmetric cell structure of ZBB. The antisymmetric cell structure is described that volume electrode which used for cathode structure can provide large surface area for improving reaction rate and surface electrode which used for anodic structure can secure solid phase deposition area. To verify the electrochemical properties and effectiveness of the structure, Cyclic

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Voltammetry (CV) measurements and cyclic operation test (charge and discharge) are carried out in 2.0 M $ZnBr_2$ electrolyte solution, respectively.

2. Electrode

Generally, carbon is used for electrode of flow battery. [7, 8] Carbon have high economical profit (cheap), high conductivity, electrochemical resistance against Br_2. [9, 10] this carbon electrode is classified by a surface electrode and volume electrode [6]. As depicted in Fig 1, in case of the surface electrode, the electrolyte flows over only the external electrode. So, the redox reaction occur only surface of the electrode. And as shown right side of the Fig 1, flow of the electrolyte runs into volume electrode and the redox reaction occur entire internal electrode. [11]. Because of above properties of the electrodes, volume electrode has a large reaction area than surface electrode. And surface electrode secure area for zinc deposition. So, because of the bromine that remains liquid phase after charge operation, it can't use surface electrode better than use volume electrode as cathode for enhancing reaction rate of the bromine.

For the purpose of certify reaction rate of the bromine, TF6 (SGL, Germany) is kind of graphite foil is used as a surface electrode and GF-031(JNTG, Korea) which is kind of a carbon felt is used as volume electrode. Each property is shown in Table 1.

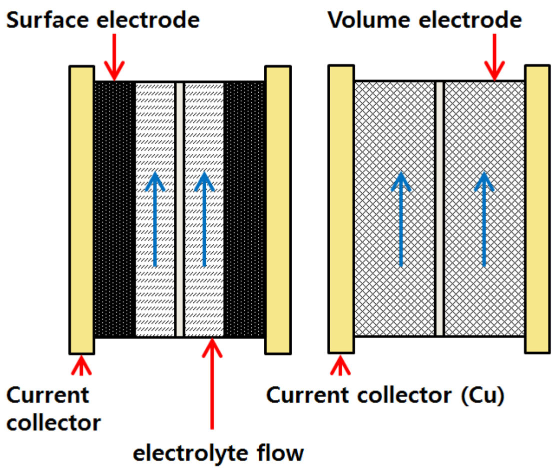


Fig. 1: Structure of the surface electrode, volume electrode.

Table 1: Caption for table goes at the top.

Class	Model Name	Company	Thickness	Electrical Resistivity
			mm	Ω·mm
Surface Electrode	TF6	SGL	0.6	0.13
Volume Electrode	JNT GF-031	JNTG	1	0.03

3. Experiment method

3.1. Cyclic Voltammetry (CV)

Cyclic Voltammetry (CV: three electrode system) is a widely used method for the study of electrochemical property of electrode [12, 13]. Surface electrode, volume electrode are used as a working electrode, Pt-wire and standard calomel electrode are used as counter electrode and standard electrode, respectively. Also, 2.0 M of $ZnBr_2$ solution is used for studying electrochemical properties of electrode. 10 mV/S of voltage scan rate and from 1.5 V to -1.5 V of voltage range are injected.

3.1.1. Cell operation test (charge and discharge operation).
Cell operation experiments are carried out for performance comparison of the following five electrode structure : (s) using surface electrode as both side of the electrode, (v) using surface electrode as an anode and using volume electrode as a cathode. In this case thickness of cathode is classified by 1mm (V-1), 2mm (V-2), 3mm (V-3), 4 mm (V-4). 2.0 M of $ZnBr_2$ solution was used to the electrolyte. [14] The charge and discharge current density is 20mA/cm^2. [15, 16] Other operating conditions are described in the table 2, in details. Coulombic efficiency (CE), Voltage efficiency (VE) and Energy efficiency (EE) are calculated by below equations.

Table 2: condition of the unit cell during charge/ discharge

Class	Value [unit]	Remarks
Flow Frame	4x5 [cm^2]	PVDF
Membrane	4x5 [cm^2]	Asahi Kasei / SF600
Active area	6 [cm^2]	
Pump	Masterflex / L/S Pump	
Current Density	20 [mA/cm^2]	
Charge Time	1 [h]	
Operating System	Won-A-Tech / WBCS3000S	

$$Voltage\ Efficiency : \frac{Discharge\ Voltage(V)}{Charge\ Voltage(V)} \times 100[\%] \quad (1)$$

$$\text{Coulombic Efficiency} : \frac{Charge\ Time(\text{sec})}{Discharge\ Time(sec)} \times 100[\%] \quad (2)$$

$$Energy\ Efficiency : \frac{Voltage\ Efficiency\ \times Coulombic\ Efficiency}{100}[\%] \quad (3)$$

4. Result and discussion

4.1. Cyclic Voltammetry (CV) result
As depicted in Fig 2, oxidation current peak value of surface electrode observed at -80.81 mA. In case of using volume electrode, -171.24mA of oxidation current peak value is observed, respectively. It means that quantity of the redox reaction of bromide cations is enhanced by large reaction surface of the volume electrode. It indicate that using volume electrode as cathode electrode can improve coulombic efficiency And bromine oxidation energy which is above area of the oxidation curve $\int_b^a f(x)\,dx$ dx]is observed that volume electrode oxidation energy is 3 times than surface electrode. And as you can see in the graph, peak current of surface electrode is large than volume electrode. It means that using surface electrode as an anode occur high coulombic efficiency. And as mentioned above, surface electrode can secure deposition area for zinc ion.

For this reason, the antisymmetric structure using surface electrode as an anode and using volume electrode as a cathode is recommended thus result of cyclic voltammetry test. Therefore, cell operation test is performed for demonstrate the result of cyclic voltammetry.

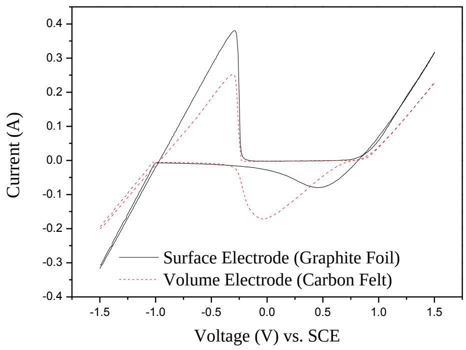
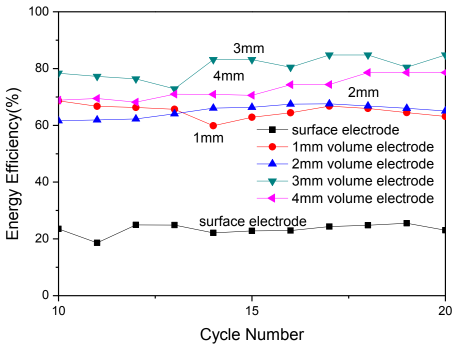


Fig. 2: Cyclic Voltagrams of (a) surface electrode, (b) volume electrode as working electrode

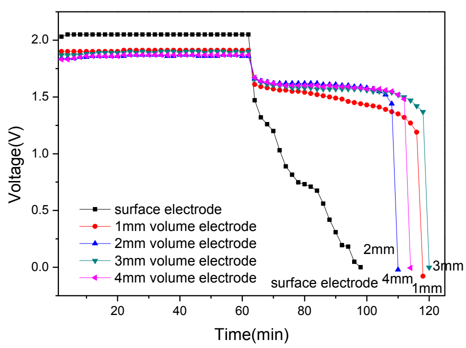
4.2. Cell operation test (charge and discharge operation) result

Cell operation experiments are carried out for compare performance with the following electrode structure: Because of volume electrode has large surface area for reaction, that's why energy efficiency of volume cathode are higher than surface electrode (average 20.49% higher). And discharge capacity using volume electrode as a cathode is longer than using surface electrode as a cathode. As depicted in Fig 3 (a), (b) and Table 3, cell which used surface electrode as a cathode shown low efficiency and low stability, as mentioned above.

(V-1), (V-2), (V-3), (V-4) are tested for optimizing. As a result, (V-3) is the best solution for ZBB. Because, (V-3) has highest energy efficiency and coulombic efficiency (discharge capacity). Because, the thicker volume electrode is used, the higher coulombic efficiency is observed. But, (V-4) has lower coulombic efficiency than (V-3). It is due to the fact that bromine reaction is higher at (V-3). Accordingly, this indicates that (V-3) is used for high energy efficiency.



(a)



(b)

Fig. 3: (a) energy efficiency, (b) voltage curve(11th) of each cathode

Table. 3: Average efficiencies of each cathode (20cycle)

Efficiency	Surface Electrode	Volume Electrode (thickness)			
		1mm	2mm	3mm	4mm
Coulombic	56.26	72.89	74.60	83.76	81.80
Voltaic	36.84	73.96	79.59	80.93	83.60
Energy	20.49	53.90	59.38	69.67	68.05

5. Conclusion

In this paper, CVs and cell-operation experiments using 2.0 M of $ZnBr_2$ solution are carried out for optimizing proper electrode structure in Zinc Bromine flow Battery (ZBB). The CV experiment has shown that the surface electrode (graphite foil) has the highest zinc oxidation current peak, and volume electrode (carbon felt) has the highest bromide current peak. In addition, cell operations have demonstrated that using volume electrode as a cathode has highest coulombic efficiency by large reaction surface. Hence, a solution to the problem encountered in the ZBBs is found.

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