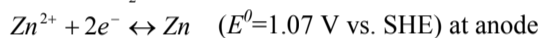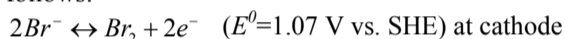# Charge Transfer Resistance Reduction by Bromine Complexation in Zinc/Bromine Flow Battery

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For last several decades, electrical energy storage as pollution-free operation and flexible energy source to meet the ever-changing energy supply/demand has raised vivid interest [1]. As the many policies are focused on the efficient use of renewable energy and smart grid construction, the scale and stability in the energy storage has emerged as a major issue. From this perspective, the redox flow battery (RFB) is one of the most viable alternatives. For example, RFB in the range of 10 kW-10 MW is the most competitive in terms of cost, flexibility, rapid response and safety over other secondary batteries such as lithium ion and sodium sulfur batteries [2]. RFB takes a variety of forms depending the employed redox couple: all vanadium(VFB), Zinc/bromine(ZBB), iron/chromium and so on [b]. Of these RFBs, the ZBB is one of the most viable alternatives based on its higher energy density (70 Wh/kg) and lower cost [3]. The main reactions in both electrodes of the ZBB system are as follows:

$2Br^- \leftrightarrow Br_2 + 2e^-$ (E^0=1.07 V vs. SHE) at cathode

$Zn^{2+} + 2e^- \leftrightarrow Zn$ (E^0=1.07 V vs. SHE) at anode

The ZBB is characterized in that the Br_2 gas occurs at the anode. Various quaternary ammoniums are used to capture the Br_2 gas in the oily complex phase because this gas phase may cause the crossover lowering the current efficiency. Therefore, the cathodic electrolyte forms a very complicated composition including water phase and oily complex phase (liquid and solid sedimentation). This complex composition makes the systematic analysis of electrode reaction difficult.

In this study, in-situ electrochemical impedance analysis was performed to elucidate the understanding on the electrode reaction. Figure 1 shows the schematic diagram of experimental setup including a single cell and two impedance cells with active area of 35 cm^2 and 4.6 cm^2, respectively.
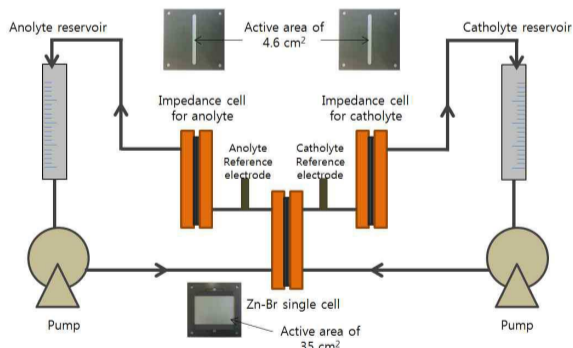

Figure 1. Schematic diagram of experimental setup.

The carbon plastic composite (CPC) was used for both the anode and cathode electrodes. While the anode electrode is characterized by the smooth surface with low active area, the cathode electrode was coated by the carbon active layer to increase the active area (> 1500 cm^2/cm^2). Figure 2 present the impedance analysis results with various state of charge (SOC) for the first cycle of charge-discharge test.
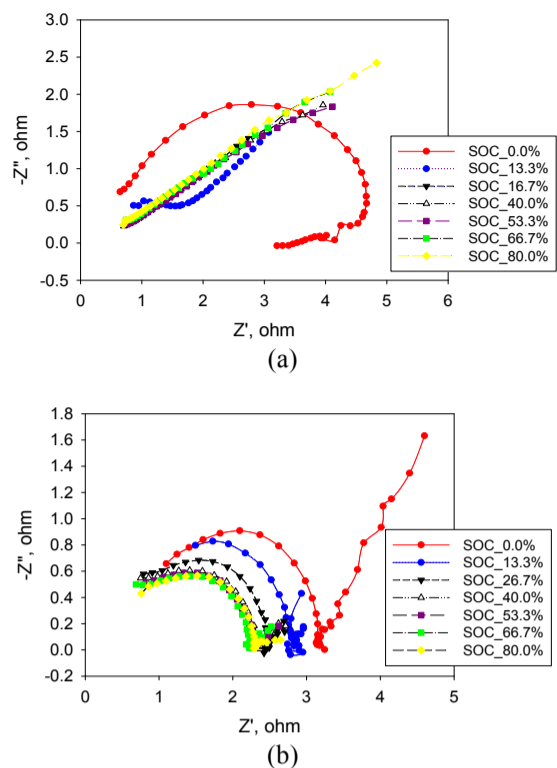

(a)

(b)

Figure 2. Electrochemical impedance analysis results for the anode (a) and cathode (b) electrolytes with various SOCs for the first cycle of charge-discharge test.

The impedance of anolyte with SOC=0% was somewhat different from those with different SOCs. This may be because zinc dendrite was nucleated and grown on the electrode surface at SOC > 0%.

From the impedance analysis of catholyte, the charge transfer resistance decreased from 2.13 ohm to 1.39 ohm as the SOC increase from 0% to 80.0%. Such a reduction in charge transfer resistance may be associated with poly-bromide complexes. The Polybromide complexes can be assumed to facilitate the desorption of Br_2 gas from the CPC electrode.

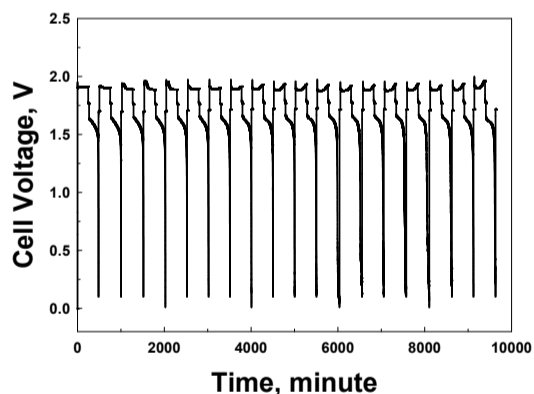Figure 3 shows the charge-discharge cycle test for this single cell.

Figure 3. Charge-discharge cycle test for Zn/Br RFB single cell.

References

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3. Q. Lai, H. Zhang, X. Li, L. Zhang, and Y. Cheng, J. Power Sources, 234, 1 (2013).