



Critical rate of electrolyte circulation for preventing zinc dendrite formation in a zinc–bromine redox flow battery



Hyeon Sun Yang ^a, Jong Ho Park ^{a,b}, Ho Won Ra ^c, Chang-Soo Jin ^a, Jung Hoon Yang ^{a,d,*}

^a Energy Storage Laboratory, Korea Institute of Energy Research, 152 Gajeong-ro, Yuseong-gu, Daejeon 34129, Republic of Korea

^b Department of Chemical Engineering, Hanyang University, 222 Wangsimni-ro, Seongdong-gu, Seoul 04763, Republic of Korea

^c Clean Fuel Laboratory, Korea Institute of Energy Research, 152 Gajeong-ro, Yuseong-gu, Daejeon 34129, Republic of Korea

^d Department of Renewable Energy Engineering, University of Science and Technology, 217 Gajeong-ro, Yuseong-gu, Daejeon 34113, Republic of Korea

HIGHLIGHTS

- Polybromide and aqueous phases led to different kinetics of Br/Br[−] redox reaction.
- Poor mixing of the two phases caused uneven redox kinetics on positive electrode.
- Uneven reaction on positive electrode was accompanied by zinc dendrite formation.
- Zinc dendrite formation degraded battery stability.
- Therefore, a minimum circulation rate should be set to avoid poor mixing.

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ABSTRACT

In a zinc–bromine redox flow battery, a nonaqueous and dense polybromide phase formed because of bromide oxidation in the positive electrolyte during charging. This formation led to complicated two-phase flow on the electrode surface. The polybromide and aqueous phases led to different kinetics of the Br/Br[−] redox reaction; poor mixing of the two phases caused uneven redox kinetics on the electrode surface. As the Br/Br[−] redox reaction was coupled with the zinc deposition reaction, the uneven redox reaction on the positive electrode was accompanied by nonuniform zinc deposition and zinc dendrite formation, which degraded battery stability. A single-flow cell was operated at varying electrolyte circulation rates and current densities. Zinc dendrite formation was observed after cell disassembly following charge–discharge testing. In addition, the flow behavior in the positive compartment was observed by using a transparent version of the cell. At low rate of electrolyte circulation, the polybromide phase clearly separated from the aqueous phase and accumulated at the bottom of the flow frame. In the corresponding area on the negative electrode, a large amount of zinc dendrites was observed after charge–discharge testing. Therefore, a minimum circulation rate should be considered to avoid poor mixing of the positive electrolyte.

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1. Introduction

Renewable energy sources such as wind and solar power have increasingly contributed to the global energy supply over the last several years. According to the Renewable Energy Policy Network for the 21st Century's 2015 annual report, renewable energy sources supplied about 19.1% of the global final energy consumption in

2013 [1]. However, one of the biggest obstacles to their development is intermittent energy production due to dependence of renewable energy sources on the weather and time [2]. Large-capacity battery systems have received considerable attention because they have potential to efficiently regulate energy demand and supply when combined with renewable energy sources and smart grids. The redox flow battery (RFB) is one of the most viable secondary batteries in terms of cost effectiveness, response speed, and service life duration [3–5]. In particular, its independent design in terms of power and energy capacity makes it a suitable advanced system for large-capacity energy storage.

* Corresponding author. Energy Storage Laboratory, Korea Institute of Energy Research, 152 Gajeong-ro, Yuseong-gu, Daejeon 34129, Republic of Korea.

E-mail address: enviroma@kier.re.kr (J.H. Yang).

The RFB can use various species as redox couples. For example, vanadium ions with four different valence numbers can participate in the redox reaction in a vanadium RFB [3,6]. In a zinc–bromine RFB, zinc ion is reduced to zinc metal on the negative electrode, while bromine ion is oxidized to bromine on the positive electrode during charging [7–12]. Besides these examples, there are tens of other RFBs, including iron–chromium, polysulfide–bromine, zinc–cerium, and organic RFBs [3,13,14]. Among these examples, the zinc–bromine RFB is one of the most viable alternatives because of its low cost and high energy density (70 Wh kg^{-1}) [10]. However, bromine should be securely contained within the cell because it is extremely irritating to mucous membranes and internal organs. To effectively contain bromine within the electrolyte, quaternary ammonium bromides (QBr) are used [15–17]. For example, 1-methyl-1-ethylpyrrolidinium bromide can form a quaternary ammonium polybromide through complexation with several bromine molecules, lowering the Br_2 vapor pressure within the electrolyte. This polybromide complex takes the form of a nonaqueous, stable, and dense phase, which is separated from the aqueous electrolyte. Therefore, two-phase flow occurs on the positive electrode surface.

The polybromide phase can interact with the electrode surface differently from the aqueous phase. According to Bauer et al. [18], QBr combines with two bromine molecules, producing QBr_5 as the major species. According to the equivalence, the bromine/bromide ion atomic ratio is about 4 in the polybromide phase. Conversely, there are many bromide ions and few bromine molecules in the aqueous phase. This difference suggests that the polybromide and aqueous phases may respectively favor charge and discharge reactions, depending on the concentration polarization. In addition, the polybromide phase has a negative effect on the ohmic overpotential. Although polybromide is a conductive ionic salt, its conductivity is much lower than that of the aqueous phase. Furthermore, the viscosity and density of the polybromide phase is much higher than those of the aqueous phase. The difference in these physical properties weakens the mixing intensity between two phases, which strongly influences the electrochemical performance on the electrode surface.

Inhomogeneous mixing of the polybromide and aqueous phases may cause uneven redox kinetics on the positive electrode surface. The Br/Br^- redox reaction is coupled with the zinc deposition reaction in the zinc–bromine RFB. In other words, the uneven redox reaction on the positive electrode may be accompanied by nonuniform zinc deposition and formation of zinc dendrites, which degrade the battery stability.

Therefore, understanding the flow characteristics is needed to improve battery performance and stability. One of the most important variables that determine the flow behavior is the electrolyte circulation rate. However, there have been few studies on its effect on zinc–bromine RFB performance. In the present study, a single-flow cell was operated at varying electrolyte circulation rates and current densities. The resulting data were analyzed with focus on the formation of zinc dendrites. In addition, a transparent version of the cell with a structure similar to the single-flow cell was used to observe the flow behavior inside the cell. The flow characteristics were interpreted in relation to zinc dendrite formation.

2. Experimental

2.1. Charge–discharge experiments

A charge–discharge test was performed in a single-flow cell (Fig. 1) composed of graphite bipolar plates with an active electrode area of 35 cm^2 , PTFE (polytetrafluoroethylene) flow frames, and a porous separator (Asahi Kasei Co., Ltd., Japan). Polyethylene mesh

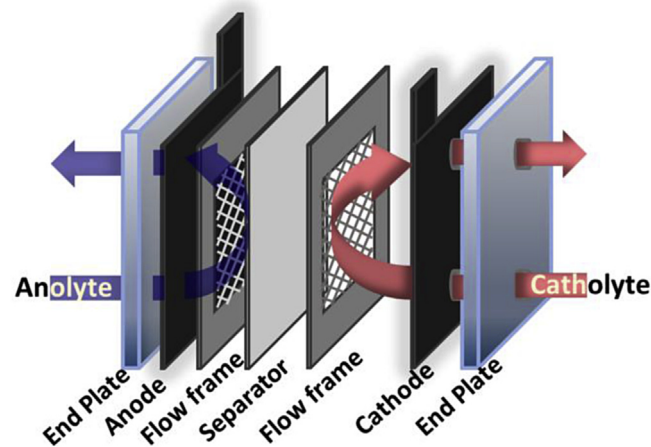


Fig. 1. Schematic diagram of the structure of the single-flow cell. The cell consists of two graphite polar plates, two polytetrafluoroethylene flow frames, two polypropylene meshes, a porous separator, and end plates.

with a thickness of 0.75 mm was inserted into the PTFE flow frame to promote turbulence. Graphite bipolar electrodes with and without an activated carbon layer were used as positive and negative electrodes, respectively.

Both the initial positive and negative electrolytes consisted of an electrolyte solution of 2.25 M ZnBr_2 , 0.5 M ZnCl_2 , 5.0 mL L^{-1} bromine, and 0.8 M 1-methyl-1-ethylpyrrolidinium bromide in deionized water. This electrolyte solution was purchased from Hanchang Co., Ltd (Korea). Using a peristaltic pump, we circulated each electrolyte (30 mL) at flow rates of 50–150 mL min^{-1} , which correspond to superficial velocities of 0.6–1.8 cm s^{-1} and Reynolds numbers of 14.1–42.4 within the flow frame without considering any internal structures such as mesh and zinc deposit.

The single-flow cell was operated at current densities of 15, 20, and 25 mA cm^{-2} . The cell was charged to a predetermined capacity of 2.88 A h and then discharged to 0.1 V by using a Maccor Series 4000 battery testing system. A charge capacity of 2.88 A h corresponds to a state of charge (SOC) of 40% based on the theoretical capacity of both positive and negative electrolytes.

2.2. Electrochemical analysis

To investigate the electrochemical characteristics of the positive electrolyte at 40% SOC, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed with a three-electrode system. Glassy carbon, platinum wire, and Ag/AgCl (3.0 M) electrodes were used as the working electrode, counter electrode, and reference electrode, respectively. The effective area of the working electrode was 0.0707 cm^2 . After 30 mL of the positive electrolyte was charged to 2.88 A h in the single-flow cell, it was withdrawn and left to stand to allow clear separation of the aqueous and oily polybromide phases. To compare the Br^-/Br redox kinetics in the aqueous and polybromide phases, the working electrode was positioned in each phase prior to CV and EIS. For the CV test, the potential scan was started at the open-circuit voltage in the positive voltage direction and then reversed at a scan rate of 1 mV s^{-1} . EIS was performed within the frequency range of 100 kHz to 10 mHz with the potential perturbations of amplitude 10 mV at 0.85 V and 0.79 V versus the reference electrode.

2.3. Analysis of flow characteristics

To observe the flow characteristics within the single-flow cell, a

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