Journal of Power Sources 275 (2015) 294–297

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

Effect of a surface active agent on performance of zinc/bromine redox flow batteries: Improvement in current efficiency and system stability

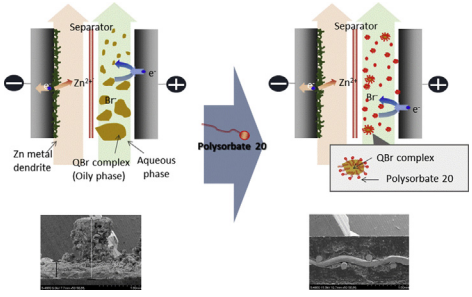
Jung Hoon Yang [a, *], Hyeon Sun Yang [a], Ho Won Ra [b], Joonmok Shim [a], Jae-Deok Jeon [a]

[a] Energy Storage Laboratory, Korea Institute of Energy Research, Daejeon 305-343, Republic of Korea
[b] Clean Fuel Laboratory, Korea Institute of Energy Research, Daejeon 305-343, Republic of Korea

HIGHLIGHTS

- The effect of Polysorbate 20 on Zn/Br RFB performance was investigated.
- The surfactant prevented uneven dissolution of Zn during discharge.
- Current efficiency decrease with cycle number was improved with Polysorbate 20.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 September 2014
Received in revised form
18 October 2014
Accepted 25 October 2014
Available online 8 November 2014

Keywords:
Polyoxyethylene (20) sorbitan monolaurate
Surface active agent
Current efficiency
Polybromide complex
Zinc dendrite

ABSTRACT

A sustained decrease in current efficiency (CE) is a commonly observed phenomenon in a zinc/bromine redox flow battery. To circumvent this problem, that is, to improve the CE and system stability of the redox flow battery, a surface active agent (SAA), polyoxyethylene (20) sorbitan monolaurate, is introduced as an additive. To investigate the effect of this SAA on the cell performance, polarization testing is performed and the electrode surface is observed after 32 cycles of charge–discharge testing. Adding the SAA facilitates catholyte mixing, leading to an effective reduction of bromine during discharging.

1. Introduction

Electrical energy storage technology has received increasing attention as an important complement to meet the ever-changing energy supply/demand and for using renewable energy efficiently [1–3]. Therefore, many policies are focused on large-capacity battery systems rather than on small-capacity ones for use in electronic equipment. Among large-capacity battery systems, the redox flow battery (RFB) is one of the most viable and economical options with respect to capacity and stability. The RFB is the most competitive, especially across the range of 10 kW to 10 MW, owing to its intrinsic advantages such as flexibility, rapid response, cost effectiveness, low operating temperature, and safety [4–7].

RFBs generally consist of electrodes, a membrane/separator, negative and positive electrolytes (redox couple, supporting electrolyte, and solvent), pumps to circulate these electrolytes, and electrolyte reservoirs. Depending on the type of redox couple employed, RFBs are classified into different types, including zinc/

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

http://dx.doi.org/10.1016/j.jpowsour.2014.10.208
0378-7753/

bromine (ZBB) [8,9], all vanadium [10,11], and iron/chromium [12], to name a few.

The ZBB is characterized by its higher energy density (70 Wh kg^{-1}) and lower cost compared with other types of RFBs [13]. According to Annika Larsson [14], current technology makes ZBBs above the 100 kW-scale economically feasible. In addition, numerous large-scale demonstration projects based on ZBBs have been implemented across the United States. The main reactions occurring at the two electrodes of the ZBB system are as follows:

$$2Br^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Br_2 + 2e^- \quad \left(E^0 = 1.07\text{V vs. SHE}\right) \quad \text{at the cathode}$$

$$Zn^{2+} + 2e^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Zn \quad \left(E^0 = -0.76\text{V vs. SHE}\right) \quad \text{at the anode}$$

During the charging process, the bromide ions in an aqueous catholyte solution are oxidized to bromine, which forms a new oily polybromide-complex phase in combination with quaternary ammonium cations [15,16]. During discharge, bromine captured in the oily phase is reduced to bromide ions, which are soluble in the aqueous phase, thus providing a good battery performance. Therefore, the bromine/bromide conversion at the cathode is an important factor for determining the battery performance. This complex interaction leads to electrolyte instability, resulting in a steady reduction in current efficiency (CE), thus limiting the long-term operation of ZBBs [7,17,18].

In this study, we added a small amount of a surface active agent (SAA), polyoxyethylene (20) sorbitan monolaurate (Polysorbate 20), to the electrolyte to improve the CE and system stability. To investigate the effect of this SAA in more detail, a polarization test was performed for the electrolyte with a state of charge (SOC) of 20%. The electrode surface was observed after 32 cycles of charge–discharge testing.

2. Experimental

2.1. Charge–discharge experiments

The initial anolyte and catholyte solutions had the same composition of $ZnBr_2$ (2.25 M), $ZnCl_2$ (0.5 M), bromine (5 mL L^{-1}), and 1-methyl-1-ethylpyrrolidinium bromide (0.8 M), which is a quaternary ammonium salt, in deionized water. Polysorbate 20 was added to the anolyte and catholyte solutions at three different concentrations: 0.01 wt%, 0.05 wt%, and 0.20 wt%. 30 mL of each electrolyte was circulated through a single cell with an active electrode area of 35 cm^2. The flow rate of the electrolyte was controlled at 100 mL min^{-1}. Carbon-polymer composite (CPC) electrodes with and without an activated carbon layer were used as the negative and positive electrodes, respectively. The CPC consisted of polypropylene and conductive carbon (Lotte Chemical Co., Ltd). The cell was charged to 2.88 A·h and then discharged to 0.01 V at a current density of 20 mA cm^{-2} using a Maccor Series 4000 battery test system. The entire test was performed at room temperature.

2.2. Polarization test

The cathodic and anodic polarization was measured around the approximate open circuit voltage of 0.82 V. A three-electrode system was employed, consisting of a glassy carbon working electrode with an effective area of 0.0707 cm^2, a platinum wire counter electrode, and a Ag/AgCl reference electrode. The overpotential was increased to 0.20 V with a step potential of 1.0 mV at a scan rate of 1.0 mV s^{-1} and then decreased to −0.20 V under the same conditions. The current was recorded at each overpotential.

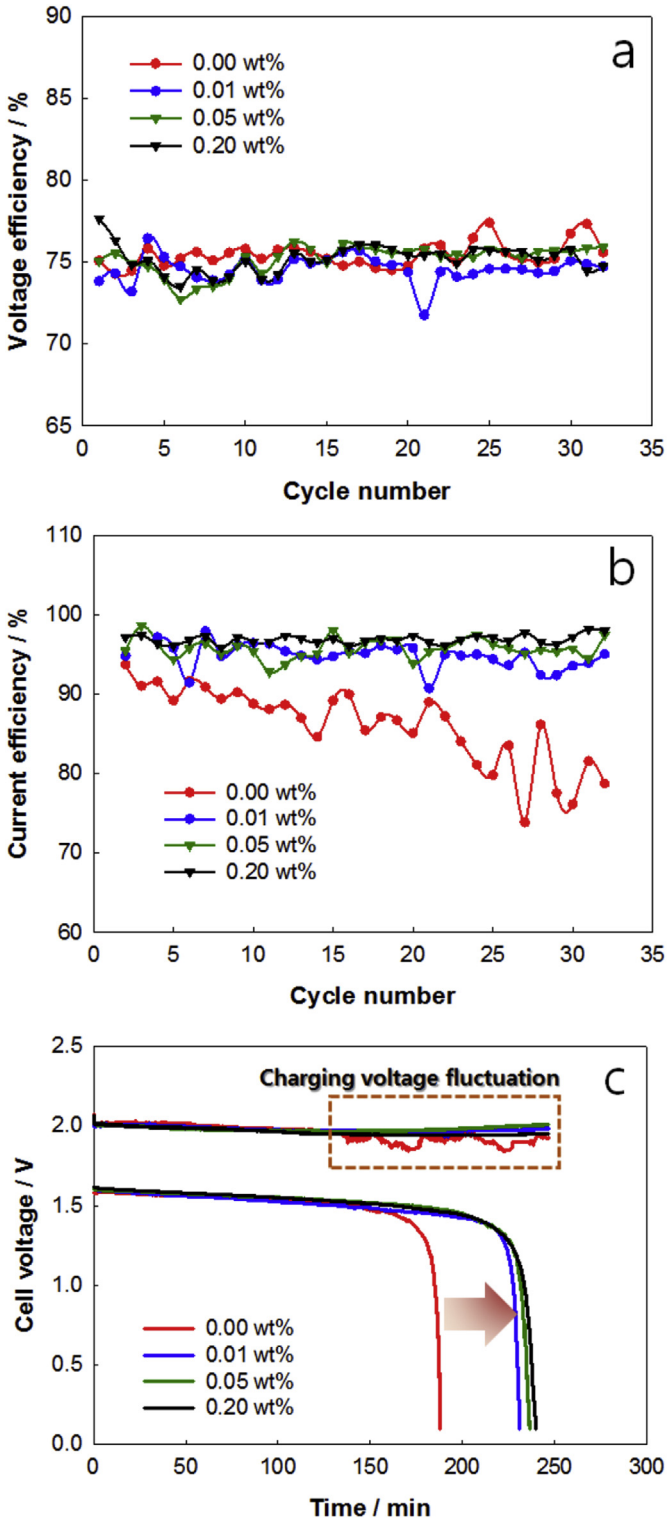


Fig. 1. Charge–discharge performance of cells with different Polysorbate 20 concentrations: (a) voltage efficiency, (b) current efficiency, and (c) charge–discharge curve at the 30th cycle.