



Development of rechargeable lithium–bromine batteries with lithium ion conducting solid electrolyte



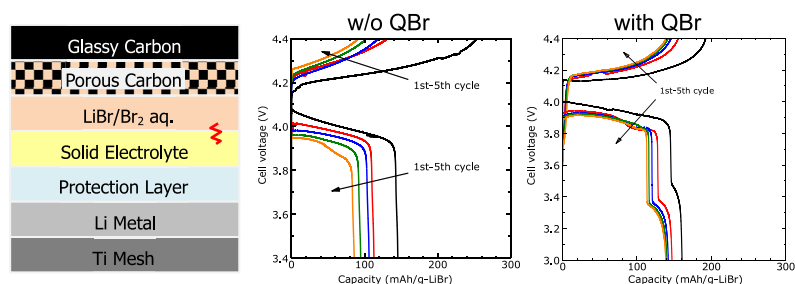
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HIGHLIGHTS

- Influence of Br_2 formation in lithium–bromine batteries (LBBs) is investigated.
- Br_2 increases interfacial resistance on the solid electrolyte.
- Addition of quaternary ammonium bromide suppresses the interfacial resistance.
- The reduced interfacial resistance improves cycleability of LBBs.

GRAPHICAL ABSTRACT



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ABSTRACT

Electrochemical performances of a prototype lithium–bromine battery (LBB) employing a solid electrolyte is investigated. The discharge capacity decreases with repeating charge/discharge cycles. Electrochemical impedance analysis reveals that the capacity fading is mainly due to increase in the interfacial resistance between an aqueous active material solution and a solid electrolyte. Based on the results of symmetric cells and structural analysis of the surface of the solid electrolyte immersed in Br_2 solutions, it is suggested that a Li^+ -depletion layer is formed on the surface of the solid electrolyte as a result of contact with bromine. Addition of tetraethylammonium bromide (TEABr) depresses the interfacial resistance, which results in improved cycleability. LBB with 1.0 M LiBr and 0.25 M TEABr shows discharge capacity of 139 mAh/g-LiBr and Coulombic efficiency of 99.6% at 5th cycle.

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1. Introduction

Energy storage devices that exceed conventional lithium ion batteries have attracted much attention because of their potential application to electric vehicles and load leveling of renewable energy. New energy storage devices are required to exhibit much higher performance in terms of cyclic life, cost, and reliability as well as energy density and power density than current devices such as lithium ion batteries. Recently, several studies have been

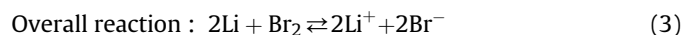
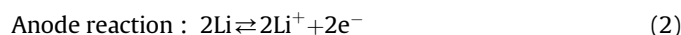
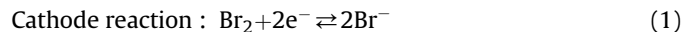
reported on a new class of batteries employing solution based (mostly aqueous) active materials coupled with a solid electrolyte that also plays a role of separator [1–10]. In these works, advantages of high theoretical capacity and good cycle performance of active material solutions are demonstrated. When we think of the solution based batteries, it should be noted that energy density is shown on the basis not of active materials but of a cell or a whole battery system, because solution based batteries contain large amount of solvent to dissolve active materials.

Zinc–bromine (Zn–Br_2) batteries, which are generally used as a flow battery, are known as one of batteries which have high energy density (433 Wh/kg-cell). However, Zn–Br_2 batteries have suffered

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from some problems such as low working potential of 1.8 V, Br₂ crossover and dendrite deposition on anode electrodes on charging that may cause short-circuit. To overcome these problems of Zn–Br₂ batteries, we have developed lithium–bromine battery (LBB) employing Li-metal anode, a solid electrolyte (SE) and a Br₂/Br[−] redox couple in an aqueous active material solution (AAM). The reactions are described as follows:



A solid electrolyte separates aqueous active material solution from Li metal and also hinders short-circuit. In addition, LBB is expected to exhibit high working voltage of ca. 4.1 V and higher energy density (>650 Wh/kg and >1000 Wh/L) than current LIB (at most 200–300 Wh/kg) and Zn–Br₂ battery, because Li metal is used as a negative electrode. Recently, superb performance of LBB has been successively reported by two groups [9,10]. The reversible capacity was more than 300 mAh/g-Br and their charge/discharge cycle was very stable. However, it should be mentioned that, in these reports, AAM consists of at most 2 M “active” LiBr and 7 M “inactive” Br[−] to stabilize Br₂ formed on charging through the reaction:



Although the solubility of LiBr is as high as 160 g/100 g-H₂O at 20 °C (~10 M), that of Br₂ is only 3.1 g/100 g-H₂O at 20 °C. Due to the large difference in the solubility between LiBr and Br₂, when concentrated LiBr aqueous solution is used as an LBB, a certain amount of free Br₂ is produced on charging the LBB, which may cause degradation of components of the LBB because of high vapor pressure and strong oxidative nature of Br₂. It is supposed that only 30% LiBr is used as an active materials in Refs. [9,10], which can be explained well with the equilibrium constant of Eq. (4), 16.1 M^{−1} [11,12]. Based on this equilibrium constant, the extra Br[−] that was 3.5 times higher in concentration than active LiBr was needed in the case of Ref. [10], which would reduce the concentration of Br₂ to below 0.024 M. However, this limitation results in the low energy density of ca. 150 Wh/kg and 240 Wh/L in terms of a whole cell. In order to realize the very high energy density mentioned above, it is needed that almost all LiBr in concentrated AAM is used as “active” materials. When an LBB is operated with such a condition, Br₂ would be surely produced. However, there has been no report on influence of the Br₂ formation on LBB performance. In this study, we assembled prototype LBBs and investigated their electrochemical performances with a condition in which Br₂ is formed. In addition, we investigated properties and resistances of each polarization element by assembly of symmetric cells with different concentrations of aqueous active material.

2. Experimental

2.1. Lithium–Bromine Battery

As shown in Fig. 1, a prototype LBB was assembled. The cathode part was composed of porous carbon (120 nm in pore diameter) coated on glassy carbon and 1.0 M LiBr aqueous solution (200 μl) aqueous active material. The 1.0 M LiBr aqueous solution was prepared using anhydrous LiBr (>95%, Kishida Chemical Co., Ltd.). The porous carbon was fabricated by using a colloidal crystal templating method as described in details elsewhere [13–17]. Powdery porous carbon was dispersed in a 10 wt% solution of polyvinylidene fluoride

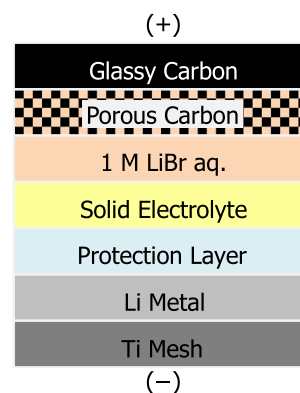


Fig. 1. The structure of a prototype LBB.

in *N*-methyl-2-pyrrolidone (Kureha Corp.) to make slurry. A drop of slurry was coated on a glassy carbon electrode with a diameter of 6 mm and dried at 70 °C under vacuum overnight. Typically, surface area of the porous carbon on an electrode was 1500 cm². Sheets of NASICON-type SE in the system Li_{1+δ}(Al, Ti, Ge)₂(Si, P)₃O₁₂ were supplied by OHARA Inc. (Li⁺ conductivity: 1 × 10^{−4} S cm^{−1}, thickness: 150 ± 20 μm). Li foil (0.1 mm in thickness, Honjo Metal Co., Ltd.) was used as an anode. An electrolyte solution of 1.0 M LiPF₆ in a mixed solvent of ethylene carbonate and dimethylcarbonate (1:1 by volume, Kishida Chemical Co., Ltd.) was used to prevent SE from direct contact with Li metal (protection layer). A cell was composed of outer cases (made of poly(tetrafluoroethylene)) and O-rings to avoid leakage of AAM, Br₂ and protection layer. First, anode parts of a cell were assembled in an Ar-filled glove box. Then, 200 μl of aqueous active material solution was introduced to the cathode side of the cell outside the glove box. Finally, a porous carbon electrode was fixed.

Galvanostatic charge/discharge tests were conducted at a current rate of 0.28 mA/cm² (based on SE area, which corresponding to C/25 based on weight of LiBr) in a potential range from 4.4 V to 3.4 V on an 8-channel battery tester (HJ1001SM8, Hokuto Denko Corp.). Before the charge/discharge tests of LBB, it was confirmed that oxygen evolution reaction (OER) was negligible by using 1 M LiNO₃ aqueous solution instead of LiBr. Although the OER should occur for higher than 3.8 V vs. Li/Li⁺ at pH = 7. However, the overpotential of OER on carbon electrode is very large. For 1 M LiNO₃, no current was observed in cyclic voltammetry, which is consistent with Ref. [9]. And also, the resistances of LBB cells after each charge and discharge were measured by electrochemical impedance spectroscopy (EIS) with an oscillation voltage of 10 mV in a frequency range from 500 kHz to 0.01 Hz using a multi-channel potentiogalvanostat S1470 E with a frequency response analyzer S1255B (Solartron Analytical). Recorded spectra were simulated and fitted with an equivalent circuit by a software ZView (Scribner Associates Inc.).

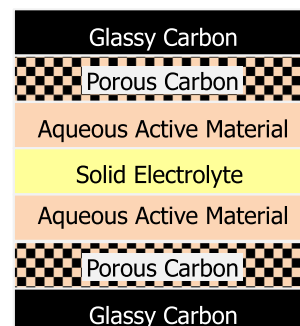


Fig. 2. A symmetric cell used to study electrochemical polarization in LBBs.

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