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Performance and Degradation of A Lithium-Bromine Rechargeable Fuel Cell Using Highly Concentrated Catholytes

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ABSTRACT

Lithium-air batteries have been considered as ultimate solutions for the power source of long-range electrified transportation, but state-of-the-art prototypes still suffer from short cycle life, low efficiency and poor power output. Here, a lithium-bromine rechargeable fuel cell using highly concentrated bromine catholytes is demonstrated with comparable specific energy, improved power density, and higher efficiency. The cell is similar in structure to a hybrid-electrolyte Li-air battery, where a lithium metal anode in nonaqueous electrolyte is separated from aqueous bromine catholytes by a lithium-ion conducting ceramic plate. The cell with a flat graphite electrode can discharge at a peak power density around 9 mW cm^{-2} and in principle could provide a specific energy of 791.8 Wh kg^{-1}, superior to most existing cathode materials and catholytes. It can also run in the regenerative mode to recover the lithium metal anode and free bromine with 80-90% voltage efficiency, without any catalysts. Degradation of the solid electrolyte and the evaporation of bromine during deep charging are challenges that should be addressed in improved designs to fully exploit the high specific energy of the liquid bromine. The proposed system offers a potential power source for long-range electric vehicles, beyond current Li-ion batteries yet close to envisioned Li-air batteries.

1. Introduction

Li-ion batteries have powered the revolution in portable electronics and tools for decades, but their initial penetration into the market for electrified transportation has so far only achieved products that are very expensive or short in driving range [1]. Lithium-air batteries are considered among the most promising technologies beyond Li-ion batteries [2–4], since the very high theoretical specific energy may reduce the unit cost down to less than US$150 per kWh, while increase the driving range of an electric vehicle to more than 550 km [5]. However, just as that Li-ion technology experienced many problems at its advent decades ago, Li-air technology is currently facing several challenges [6]. For nonaqueous Li-air batteries composed of lithium metal, organic electrolyte and porous air electrode, a robust electrolyte resistant to the attack by the reduced O_2^- species is yet to be developed to enable highly reversible cycling [4,5]. For aqueous and hybrid Li-air batteries that adopt solid-state electrolytes to protect the nonaqueous electrolyte and lithium metal anode from contamination, it is still quite challenging to improve the poor kinetics of the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) simultaneously [7] and economically [4]. To circumvent this challenge, Goodenough et al. [8–10] and Zhou et al. [11] independently extended the hybrid Li-air battery to hybrid Li-redox flow batteries by flowing through liquid catholytes instead of air [12,13]. The key concept of flowing electrodes is also exploited in semi-solid flow batteries [14], redox flow li-ion batteries [15,16], and flowable supercapacitors [17].

One of the most attractive features of flow batteries is the decoupling of power and energy, which enables more flexible system customization, either by increasing the number of electrode pairs for higher power output, or by increasing the size of the tank and concentration of electrolytes to store more energy [13]. For electric vehicles with limited on-board space to store electrolytes, high solubility of the active species becomes especially important. Recognizing that iodine has an extremely high solubility in iodide solutions, Byon et al. investigated the performance of dilute iodine/iodide catholyte in hybrid-electrolyte lithium batteries both in the static mode [18] and the flow-through mode [19], in which the end-of-discharge product is LiI. Concentrated iodine/iodide solution was also employed in a recent

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zinc-polyiodide flow battery, producing ZnI_2 at the end of discharge [20]. Comparing these two reports, although LiI and ZnI_2 solutions have similar capacity at their solubility limits, the use of a lithium anode increases the voltage almost three-fold, thus providing much higher specific energy. Table 1 summaries the theoretical specific energies of catholytes used in several state-of-the-art flow or static-liquid batteries, where LiBr solution emerges as the best candidate, having almost twice the specific energy of the aqueous Li-air battery using alkaline catholyte (LiOH).

This extraordinary property has started to attract the attention of researchers to develop various Li-Br batteries. Such systems always involve a liquid-solid-liquid hybrid electrolyte, in order to accommodate the nonaqueous and aqueous electrolytes. During discharge, lithium metal in the nonaqueous electrolyte is oxidized into lithium ions ($Li \rightarrow Li^+ + e^-$), which migrate toward the cathode, while electrons travel through the external circuit to reach the cathode. At the surface of cathode, bromine is reduced by the incoming electrons to bromide ions ($Br_2 + 2e^- \rightarrow 2Br^-$), followed by fast complexation with bromine to form more stable tribromide ions ($Br^- + Br_2 \leftrightarrow Br_3^-$). The reactions are reversed during recharging. Zhao et al. fabricated a static Li-Br battery with a solution of 1 M KBr and 0.3 M LiBr, which was charged to 4.35 V then discharged at various electrochemical conditions [23]. The maximum power it could deliver within the safety window was $1000\,W\,kg^{-1}$, equivalent to $5.5\,mW\,cm^{-2}$ if calculated with their loading density of LiBr ($5.5\,mg\,cm^{-2}$). Chang et al. paired a protected lithium metal anode [26] with a small glassy carbon electrode (3 mm diameter) to test the performance of 0.1 M Br_2 in 1 M LiBr and 1 M Br_2 in 7 M LiBr solutions, respectively. The latter provided a peak power density of $29.67\,mW\,cm^{-2}$ at ~2.5 V [27]. In the development of a better Li-Br battery, Takemoto and Yamada found that degradation of the solid electrolyte ceramic plate is the major source of deterioration of the cell performance. Their careful analyses on samples soaked in dilute bromine/bromide solutions for 3 days suggested the development of a Li-ion depletion layer in the solid electrolyte plate [28].

Given the strongly fuming and oxidative nature of bromine, it is understandable that previous work has only considered dilute electrolytes. Indeed, the high vapor pressure of bromine that builds up in a closed static liquid cell can easily rupture the ceramic separator. Such problems can be avoided in a flow cell, but a practical way of utilizing the high specific energy of lithium-bromine chemistry has yet to be proposed and demonstrated, using highly concentrated bromine/bromide catholytes.

In this paper, we design and fabricate a lithium-bromine fuel cell; explore the feasibility of using highly concentrated bromine catholytes of six different compositions of LiBr and Br_2, representing different states of charge (SOC) associated with 11 M LiBr solution by conservation of elemental bromine; and examine the degradation of the rate-limiting component, the lithium ion conducting solid electrolyte, by scanning electron microscopy and electrochemical impedance spectroscopy. Our results suggest that a properly designed rechargeable Li-Br fuel cell system has the potential to power long-range electric vehicles.

2. Experimental Section

2.1. Fuel Cell Design and Fabrication

The structure of the fuel cell is schematically shown in Fig. 1, which is similar to the hybrid aqueous Li-air battery [29], where lithium metal in nonaqueous electrolyte is separated from aqueous catholytes by a solid electrolyte (Li_2O-Al_2O_3-SiO_2-TiO_2-GeO_2-P_2O_5, LATP, $10^{-4}\,S\,cm^{-1}$, 25.4-mm square by 150-μm thick, Ohara Inc. Japan). A catalyst-free flat graphite plate is used as cathode. Catholytes flow through the cathode channel to complete the liquid-solid-liquid ionic pathway between lithium metal anode and graphite cathode. Details of the materials, design and fabrication of the fuel cell can be found elsewhere [30].

2.2. Catholytes Preparation

Theoretically, the fully discharged catholyte should not contain any Br_2 for further reduction reaction. It therefore must be pure LiBr solution. To avoid unexpected precipitation due to temperature fluctuations, we chose not to use the saturated LiBr solution (close to12 M), but the slightly more dilute option, 11 M LiBr aqueous solution, as the end-of-discharge catholyte. And according to the conservation of elemental bromine, we prepared 1 M Br_2 in 9 M LiBr (1 M/9 M), 2 M/7 M, 3 M/5 M, 4 M/3 M and 5 M/1 M solutions as the intermediate catholytes. Note that only 5 M/1 M solution has precipitated liquid Br_2 at the bottom of the solution, since the saturated concentration of Br_2 in 1 M LiBr solution is

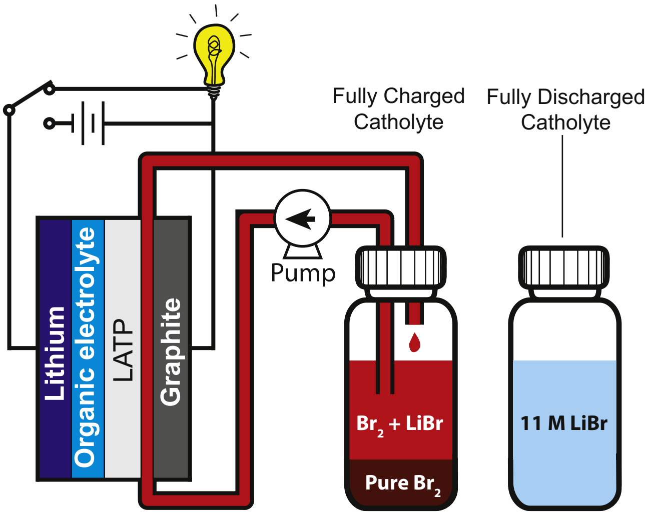

Fig. 1. Schematic illustration of the Li-Br fuel cell.

Table 1
Comparison of the specific energies of various fully discharged catholytes at their solubility limits.

Discharge product	Solubility [21,22] [g per 100 ml of water]	Molality [mol per kg of water]	Specific capacity [Ah per kg of solution]	OCV [V]	Specific energy [Wh per kg of solution]
LiBr	164.00	18.89	191.72	4.13 [23]	791.82
LiI	165.00	12.33	124.68	3.57 [18]	445.12
LiOH	12.40	5.18	123.45	3.4 [2]	419.73
$ZnBr_2$	447.00	19.85	194.51	1.85 [24]	359.84
ZnI_2	332.00	10.40	129.06	1.30 [20]	167.77
$FeCl_2$	62.50	4.93	81.33	4.06 [11]	330.19
$K_4Fe(CN)_6 \cdot 3H_2O$	28.00	0.66	13.88	3.99 [10]	55.38
Li_2S_n	–	–	–	–	170 [25]