

Miniaturisation of Zn/Br redox flow battery cell and investigation of electrode materials influence on its characteristics

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Redox flow battery has been paid attention since it has been considered as a solution for large-scale energy storage. Among redox flow batteries, this work focuses on zinc (Zn)/bromine (Br) redox flow battery. The cell of Zn/Br redox flow battery as an energy source for a sensor node of wireless sensor network systems was miniaturised. Here, the fabrication and the experimental results for performance characteristics of the miniaturised Zn/Br redox flow battery cell are reported. Moreover, the electrode materials influence on its characteristics utilising four kinds of carbon materials such as activated carbon, hard charcoal, carbon nanotubes (CNTs), and activated carbon and CNTs composite was investigated. To investigate performance characteristics, charge-discharge tests, impedance measurement, specific surface area measurement, and charge and discharge cycling life test were performed. Moreover, the morphology of electrode materials was observed. As a result, it revealed that the activated carbon electrode showed the best coulombic efficiency of 88.6% and the largest specific surface area. Moreover, it was confirmed that the activated carbon and CNTs composite electrode material has the lowest inherent internal resistance and interfacial resistance among the investigated electrode materials. In the cycling life test, the CNTs electrode showed stable capacity retention during ten cycles.

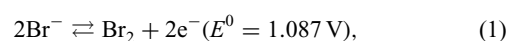
1. Introduction: Secondary battery was first proposed by Thaller [1] (National Aeronautics and Space Administration, USA) in 1974, which is also called redox flow battery. The redox flow battery is an electrochemical system to promote redox reaction of active materials by circulating electrolyte. Typical redox flow battery consists of electrolyte circulation pump, electrolyte tank, and cell likely shown in Fig. 1. In Fig. 1, we describe the schematic diagram of redox flow battery, which utilises zinc (Zn) and bromine (Br) as active materials for redox reaction. The electrodes in a cell of the redox flow battery are separated with the porous membrane. In the redox flow battery of the electrochemical energy storage system, the electric energy is stored in two separated solutions, which contain different redox couples with different electrochemical potential [2]. A variety of redox couples for redox flow battery have been studied until now. For instance, there are vanadium flow battery [3, 4], iron chromium flow battery [5], and so on. Among them, vanadium flow battery is very close to commercialisation since it has advantages in terms of life cycle and safety. In case of vanadium flow battery, there is no performance degradation because the phase change and deformation of active materials in the battery rarely occur. In other words, the charge-discharge of the vanadium flow battery is only governed by the variations of ion valence values in the electrochemical reactions of the battery. Moreover, the electrolyte of the vanadium flow battery is inflammable, which is the reason that the vanadium flow battery is the safe one. However, it has also a disadvantage that the energy density of the battery is comparably smaller than other redox flow batteries.

The redox flow battery is considered as one of future energy storages in terms of its superior cycle characteristics, design flexibility for battery capacity, use of low-cost materials, and maintenance easiness [6]. The redox couples and electrode materials have been focused in the redox flow battery and various materials have been proposed to obtain better and constant output power performance.

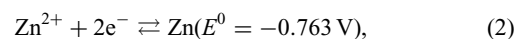
In this Letter, we propose a miniaturised redox flow battery as an energy source for a sensor node of wireless sensor network systems. As the redox couples, we employ Zn and Br because those couples have the high theoretical energy density compared with the other

redox couples used for redox flow battery. The electrochemical reactions occurring in the Zn/Br redox battery are as follows.

Positive electrode reaction



Negative electrode reaction



Net cell reaction



where E^0 means the standard oxidation–reduction potential for the standard hydrogen electrode, which is utilised as a reference electrode.

In this Letter, we report the fabrication and experimental results of our miniaturised Zn/Br redox flow battery cell represented by the cell notation: $\text{C(s)}|\text{ZnBr}_2(\text{aq}, 2\text{M})||\text{ZnBr}_2(\text{aq}, 2\text{M})|\text{C(s)}$. Furthermore, we investigated the electrode materials influence on the characteristics of miniaturised Zn/Br redox flow battery cell to find out the best performed electrode material. In characteristics measurements, we utilised four kinds of carbon materials as the electrode such as activated carbon, hard charcoal, carbon nanotubes (CNTs), and activated carbon and CNTs composite.

2. Design and fabrication: We designed a miniaturised Zn/Br redox flow battery cell. A cross-sectional view of our miniaturised Zn/Br redox flow battery cell is shown in Fig. 2. Fig. 2 shows only a battery cell without apparatus such as pumps for supplying flow of Zn/Br. It has symmetrical structure around the porous membrane. The battery cell in Fig. 2 consists of cells containing electrolyte and electrode material, membrane, and current collector. The battery cells are fabricated with glass substrates of 20 mm square. Moreover, graphite sheet is utilised for current collector, and porous material is selected as the membrane for ion exchange. The half-cell over the porous

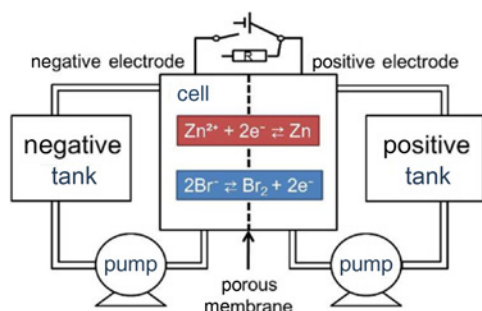


Fig. 1 Schematic diagram of a typical redox flow battery. In the diagram, Zn and Br are utilised as active materials for redox reaction

membrane in Fig. 2 is separately shown in Fig. 3 whose dimension is $10 \times 10 \times 1$ mm.

As electrode materials, we investigated four carbon materials, which are activated carbon, hard charcoal, CNTs, and composite material made of activated carbon and CNTs to reveal their performance characteristics, and to seek for suitable electrode material for our miniaturised Zn/Br redox flow battery cell.

In the cell, the mixture of 2M Zn–bromide aqueous solution (250 μ l/cell) and an electrode material powder (0.002 g/cell) are filled up. Moreover, semi-solid material such as slurry is also contained in the mixture so that the Zn/Br redox couples and electrode materials can be well adhered to the graphite sheet. The graphite sheet is employed as the lead electrode. The photograph of fabricated half-cell is shown in Fig. 4a. Each half-cell is in contact with the porous membrane. Two half-cells are assembled to one Zn/Br redox flow battery cell, which is shown in Fig. 4b. The miniaturised Zn/Br redox flow battery cells as shown in Fig. 4 are fabricated with 1 mm thick glass substrate and cell areas are formed by the usual sandblasting technique.

3. Experiments and results: We performed experiment to measure the performance of our miniaturised Zn/Br redox flow battery cell. In the experiment, only the performance of the cell as shown in Fig. 4b is characterised. In other words, we performed the experiment without the circulation apparatus such as pumps likely shown in Fig. 1 for supplying flow of Zn/Br redox couples. As a result, our performance measurement results represent the capability of the miniaturised flow battery cell itself with one full Zn/Br redox couples charging and without additional active materials supplying.

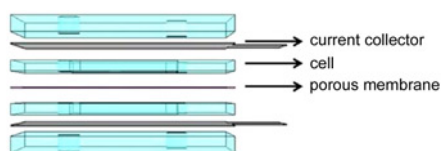


Fig. 2 Cross-sectional view of the miniaturised Zn/Br redox flow battery cell

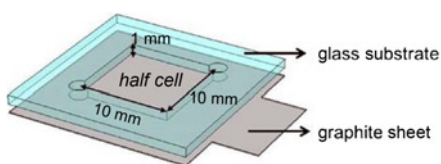
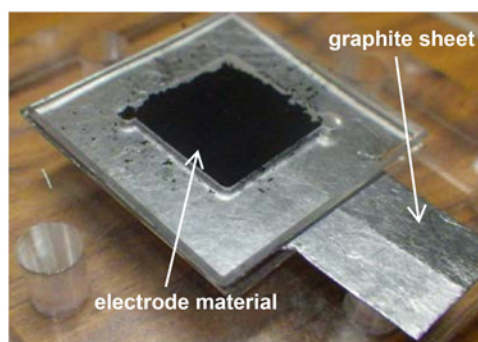
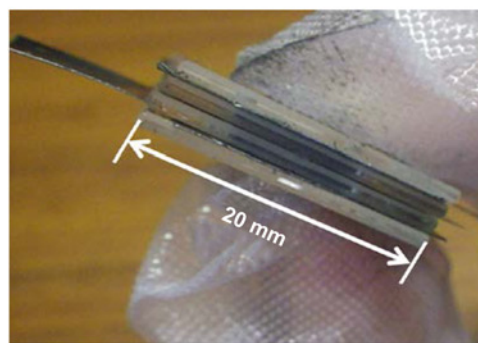


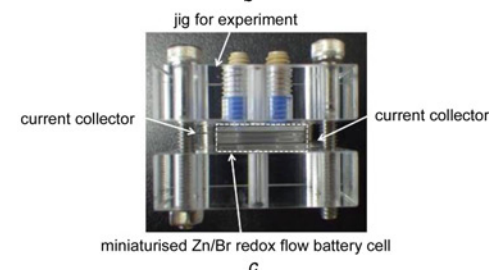
Fig. 3 Schematic view of an upper half-cell of the total battery cell shown in Fig. 2



a



b



c

Fig. 4 Photographs of fabricated miniaturised Zn/Br redox flow battery cell
a Half-cell is shown, in which Zn/Br redox couples solution, semi-solid material such as slurry, and one of electrode materials among activated carbon, hard charcoal, and CNTs, and activated carbon and CNTs composite are filled up
b Cross-sectional view of assembled miniaturised Zn/Br redox flow battery cell without the apparatus for supplying flow
c Miniaturised Zn/Br redox flow battery cell is fixed in the jig for characteristics measurement

For the characteristics measurement, we fabricated a jig with acrylic resin to fix the miniaturised Zn/Br redox flow battery cell. In Fig. 4c, the fixed miniaturised Zn/Br redox flow battery cell by the fabricated jig is shown.

In the experiment, we performed charge and discharge tests, impedance measurement, specific surface area measurement for three electrode materials, and charge and discharge cycling life test. Moreover, we also observed the morphology of four different electrode materials using scanning electron microscopy. The experiment results are as follows.

3.1. Charge and discharge tests: To confirm the basic capability of our miniaturised Zn/Br redox flow battery cell, first of all, we performed the charge and discharge tests. First, the battery cell was charged at current density of 15 mA/cm² for 900 s, and then discharged. In the discharge process, constant resistance discharge method with the resistance of 175 Ω was adopted at room temperature. The discharge voltage and time were measured until the output discharge voltage of 500 mV. Moreover, in order to clarify the electrode material influence on the basic characteristics of the miniaturised Zn/Br redox flow battery cell,

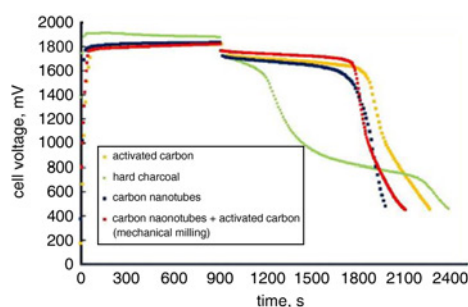


Fig. 5 Charge-discharge curves of the miniaturised Zn/Br redox flow battery cell for four different carbon electrode materials. Charged current density is 15 mA/cm^2 and discharging is performed with constant resistance until 500 mV in the test

we performed charge and discharge tests with four different carbon materials as electrode, which were activated carbon, hard charcoal, CNTs, and composite material made of activated carbon and CNTs.

In our experiment, the activated carbon and CNTs composite electrode were obtained by mixing and crashing activated carbon and CNTs through the water-cooling type planetary-motion ball-milling machine for 15 min. The ratio of activated carbon and CNTs in the composite electrode used in the experiment was 1:1.

In Fig. 5, charge and discharge experiment results are shown, which compare the charge-discharge voltage along the time for four different carbon electrode materials. As a result, in case of hard charcoal electrode material, discharge voltage of our miniaturised Zn/Br redox flow battery cell was rapidly dropped from 1700 to 800 mV, which is different to others. We suppose that it is caused by the low adsorption of Br to the electrode. However, it might be improved through the dehydration process by the thermal treatment. Among the four different carbon electrodes, the activated carbon electrode showed the best coulombic efficiency. Moreover, except CNTs electrode the two step discharge voltage drops were observed in the discharge characteristics of Fig. 5. In case of activated carbon and CNTs composite electrode, the voltage drop at 900 s was the smallest, and the discharge was performed in keeping the highest voltage. It means that the activated carbon and CNTs composite electrode material has the lowest inherent internal resistance among the investigated electrode materials.

3.2. Impedance measurement: We measured impedance spectra for three kinds of carbon electrode materials, which are activated carbon, CNTs, and activated carbon and CNTs composite. From now on, in the experiment, we do not consider the hard charcoal electrode since it showed the lowest performance in charge-discharge tests.

The impedance measurement was carried out to the miniaturised Zn/Br redox flow battery cell. For the measurement, first we charged for 500 s at 10 mA with an Interface 1000™ (Gamry

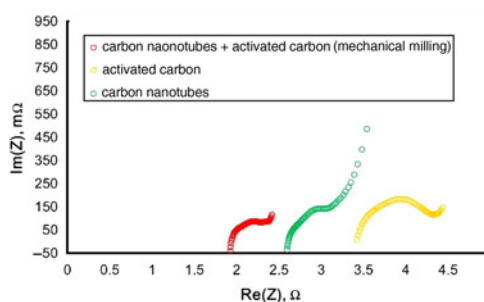


Fig. 6 Impedance spectra for the three carbon electrode materials, which are activated carbon, CNTs, and activated carbon and CNTs composite

Table 1 Specific surface area (S_{BET}) measurement results for three electrode materials

	Activated carbon	CNTs	Activated carbon + CNTs
$S_{\text{BET}}, \text{m}^2\text{g}^{-1}$	2453.51	1140.71	1322.74

Instruments, USA). The results were obtained by applying AC current of 10 mA over a frequency range of 100 kHz–1 Hz.

In Fig. 6, the impedance measurement results are represented, which consists of semi-circular and linear part. The semi-circular part and linear part correspond to charge transfer process and diffusion process in the miniaturised Zn/Br redox flow battery cell, respectively. Moreover, the extension of semi-circle gives interfacial resistance [7]. We found that the radius of the semi-circle is the largest in case of activated carbon electrode, and then CNTs, and activated carbon and CNTs composite electrodes follow. The larger the radius of the semi-circle, the lower the charge transfer rate. Though the effective surface area for the reaction of the activated carbon electrode is largest, it is considered that interfacial resistance between the activated carbon electrode and the electrolyte is the largest as well. In other words, charge transfer degradation and large interfacial resistance resulted from the state that micro-scaled particles consisting of activated carbon powder are in contact with each other.

On the other hand, though the charge transfer rate of CNTs electrode is considered as better than that of the activated carbon electrode due to CNTs bundle state, it is lower than that of the activated carbon and CNTs composite electrode. The interfacial resistance of CNTs electrode is still large due to their hydrophobicity and the lack of dangling bonds for reaction.

The interfacial resistance of the activated carbon and CNTs composite electrode is the lowest, which resulted from the mechanical milling of two materials. The activated carbon and CNTs are mixed and crashed through the mechanical milling, which give the collapse of graphite crystal and the effective reaction surface area extension. As a result, it is considered that the activated carbon and CNTs composite electrode is showing advantages taken from both activated carbon and CNTs.

For the linear part corresponding to diffusion process in Fig. 6, the CNTs electrode showed the most salient increase. Claye [8] divided and discussed the linear part into two parts. One is the line with 45° angle and another one is almost perpendicular line. The perpendicular line represents the diffusion of active materials into the CNTs bundles. Therefore, we consider that the near vertical line observed at low-frequency region in Fig. 6 for the CNTs electrode is representing the impedance caused from Br_2 or Br^- diffusion into the CNTs bundles.

3.3. Specific surface area measurement: To clarify the reaction surface area for each electrode material, the specific surface area

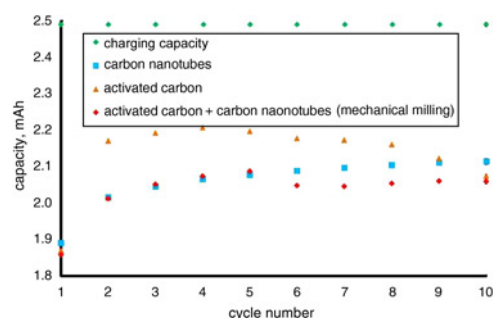


Fig. 7 Charge-discharge cycling life results of the miniaturised Zn/Br redox flow battery cell for three different carbon electrode materials

measurement was carried out for three electrode materials with an automatic specific surface area measurement apparatus Gemini 2375 (Micromeritics, USA), which employs the measurement method based on volumetric method.

The measurement results are summarised in Table 1. As a result, the activated carbon showed the largest area, and then the activated carbon and CNTs composite and CNTs follow. In case of the activated carbon and CNTs composite, the obtained value was not so larger than that of CNTs though the activated carbon and CNTs are mixed with the ratio of 1:1. We suppose that the powder particles of the activated carbon were slightly hardened during the mechanical milling process, which resulted in reduction of porosity.

3.4. Charge and discharge cycling life tests: The ten charge–discharge cycling life tests were carried out with an Interface 1000™ (Gamry Instruments, USA) at current density of 10 mA/cm². This test was conducted using three kinds of miniaturised Zn/Br redox flow battery cells, which employ the activated carbon, the CNTs, and the activated carbon and CNTs composite as their electrode materials.

The experiment results are represented in Fig. 7. The performance of the miniaturised Zn/Br redox flow battery cell with CNTs electrode was kept very stable during ten cycles. However, the average coulombic efficiency was worst than that of the miniaturised Zn/Br redox flow battery cell with the activated carbon electrode. Moreover, in case of the activated carbon and CNTs composite electrode, even though the coulombic efficiency is slightly decreased after five cycles, we obtained similar performance to that of CNTs electrode.

3.5. Morphology observation: The surface morphology of four electrode materials was characterised by an SEM observation. The observation results are summarised in Fig. 8.

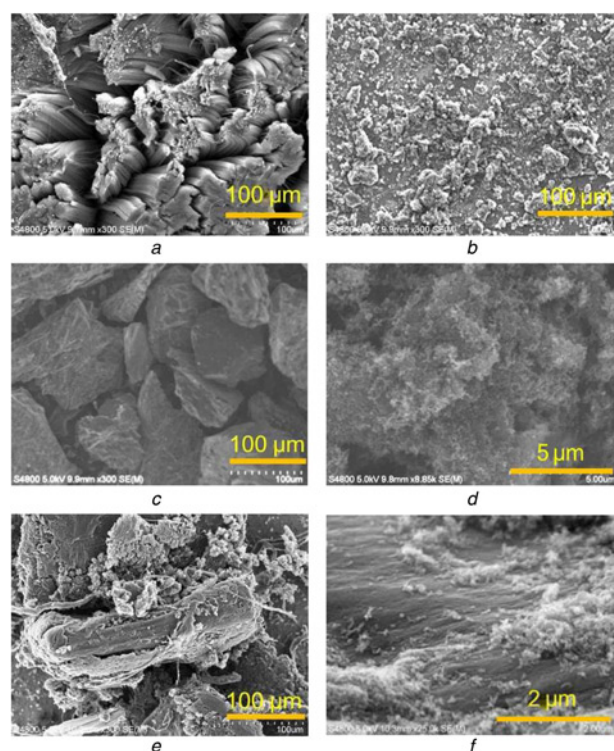


Fig. 8 Morphology of electrode materials used in the miniaturised Zn/Br redox battery cell, which is observed by the SEM

- a CNTs
- b Activated carbon
- c Hard charcoal
- d Enlarged view of the (b)
- e Activated carbon and CNTs composite
- f Enlarged view of the (e)

The particle size of hard charcoal (Fig. 8c) was the biggest among four electrode materials. On the other hand, the particle size of activated carbon (Figs. 8b and d) was smaller than that of hard charcoal, which has superior porosity as well. Those kinds of morphological characteristics are considered as the cause of the high performance showed in charge and discharge test results. Especially, it seems that a great number of pores in the activated carbon mainly contributed to the best performance in charge and discharge tests of the miniaturised Zn/Br redox flow battery cell. In other words, owing to the great number of pores, the adsorption ratio of Br on the electrode surface could be dramatically increased in case of activated carbon electrode. To increase the charge–discharge performance of a redox flow battery, the most important design parameter should be the porosity of electrode material.

The CNTs (Fig. 8a) were observed as a dense bundle state. Though CNT has also good porosity, the specific surface area between the electrode and electrolyte is smaller than that of the activated carbon electrode case as shown in Table 1 due to the bundle state of the CNTs electrode. The specific surface area between the electrode and the electrolyte is much closely related to the electrochemical reaction efficiency of the redox flow battery.

In case of activated carbon and CNTs composite electrode (Figs. 8e and f), we were able to confirm that CNT bundles are somewhat disentangled during the mechanical milling process and the condensation of CNTs is slightly moderated. Moreover, we observed that the activated carbons are adhered nonuniformly on the surface of CNTs.

In addition, we performed a qualitative analysis for activated carbon (Figs. 8b and d) and CNTs (Fig. 8a) using wavelength-dispersive X-ray spectroscopy in the electron probe microanalyser (JXA-8900RL, JEOL, Japan) to confirm their material compositions. As a result, we obtained that more than 99% of the composition of the samples was carbon: namely, there was no impurity.

4. Conclusion: We have designed and fabricated the miniaturised Zn/Br redox flow battery cell for the application to a power source of a sensor node of the wireless sensor network systems. We have also evaluated its basic performance characteristics. Moreover, we have investigated electrode materials influence on its performance characteristics through charge and discharge tests, impedance measurement, specific surface area measurement, charge and discharge cycling life tests, and morphology observation. We have achieved the coulombic efficiency of 85.3 and 88.6% in case of the miniaturised Zn/Br redox flow battery cell with CNTs and activated carbon electrodes, respectively. Moreover, we proposed a composite electrode material consisting of activated carbon and CNTs, which was prepared by mechanical milling method. It was revealed that a composite electrode has the lowest inherent internal resistance among the investigated electrode materials in this Letter.

In this Letter, though electrode materials are packed into the miniaturised Zn/Br redox flow battery cell to evaluate its basic characteristics and to investigate the influence of electrode materials on its characteristics, the electrodes especially CNTs based electrodes will be integrated in near future. To integrate CNTs based electrodes, improvement of hydrophobicity of CNTs and development of CNTs bundles fabrication method so that they are not flowed by the active materials flow are needed. Moreover, a miniaturisation of Zn/Br redox flow battery cell with circulation apparatus for active materials supply will be also considered as one of our future works, which includes the research and development of low-power consuming micropump.

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