1. Introduction

High performance batteries for mobiles, electric vehicles, backup supplies, and storage systems, have recently been in great demand. The metal air battery is superior to the lithium ion secondary battery because of no danger of ignition and its possibility of a long storage time. The metal air battery has many problems for development as a secondary battery. There are some studies about improvement of its charge-discharge properties. Takeguchi reported that the charge-discharge cycle was improved by using a layered oxide cathode. Lianga reported that the charge-discharge stability improved by using a Na cored ceramic separator for the anode. This battery has a capacity of 20 Ah and can be kept for 3 years without any electrolyte solution. It is well known that mechanical charge for the anode metal is very effective for a metal air battery. Though the metal air battery has many problems for development as a secondary battery, we think that it is a promising primary battery as a backup power supply and for emergency use.

We have been studying the development of the metal air battery using the expanded natural graphite sheet (graphite sheet) as the cathode and galvanized plate as the anode. The graphite sheets have been used for gaskets and heat radiation materials because of its high thermal conductivity, high electric conductivity, physical and chemical stability, workability, etc. It can be easily obtained in a large size with the width of 1.3 m and the length of more than 100 m. We reported that the cross section of the graphite sheet has many µm-length order gaps which are used for air passage. We think that the graphite sheets are very useful materials for a low cost and large size cathode of the metal air primary battery.

In this study, we prepared graphite sheets with various thicknesses and bulk densities, and the structure and gas permeation rate of the graphite sheets were investigated. The relationships between the thickness and density of the graphite sheets and battery properties, such as the discharge energy and voltage, have been evaluated. The metal air battery using the graphite sheet as the cathode and galvanized plate as the anode has been investigated for emergency power units.

2. Experimental

Five-cm square graphite sheets with various thicknesses and densities were prepared by pressing expanded graphite using a metallic mold. The large size standard graphite sheets with a thickness of 0.4 mm and density of 1.0 g/cm³ were prepared by a roll press machine. The starting material of flake graphite was soaked in a mixed solution of sulfuric acid (98%) with 5% hydrogen peroxide (30%) to produce sulfuric graphite of a layered compound. The expanded graphite can be obtained by heating the sulfuric graphite at 1000°C for 1 minute after preheating at 100°C and about 1 hour for drying. The graphite sheets with a thickness of 0.2–1.5 mm and density of 0.5–1.6 g/cm³ can be obtained by controlling the pressure of the press machine and weight of the expanded graphite. Figure 1 shows the relationships between the press pressure and bulk density of the 5-cm square graphite sheet and expanded graphite weight of 1.0 g. The bulk density increased with the increasing press pressure up to 10 kN, then remained constant over 10 kN. The thickness of the graphite sheet can be controlled by the weight of the expanded graphite. The thickness and density of the graphite sheet were 0.4 mm and 1.0 g/cm³ for a weight of 1.0 g and pressure of about 5 kN, respectively.

We measured the gas permeation rate in the surface direction of the graphite sheet by the differential pressure method. Figure 2 shows the measurement system equipment for the gas permeation rate. Gas flow in the surface direction of the graphite sheet sandwiched between a metal flange and acrylic plates with vent holes is indicated by the red arrow line in Fig. 2(A). Figure 2(B) shows the placement of 29 vent holes with a diameter of 3 mm on the acrylic plate. Samples were 78-mm diameter graphite sheets with various thicknesses and densities. The chamber volume and measurement time were 1.1 × 10⁻³ m³ and 1800 sec, respectively.
The gas permeation rate was calculated by dividing the product of the chamber volume and pressure change amount in the chamber by the measurement time. A different size and shape of the graphite sheets for the cell were used for the measurement, because the purpose was not to know the absolute value but to find the thickness and density of the graphite sheet’s dependence of the gas permeation rate. The internal resistance was measured by a battery tester (Hioki BT3562-01). The surface morphology and cross section of the graphite sheets were observed by a FESEM (Hitachi SU-5000) and SPM (Bruker Dimension ICON-3100). The crystal structure of the graphite sheets were observed by XRD (Rigaku Ultima-V).

Figure 3 shows the standard single cell (A) and series connected structure with two cells (B) of the metal air battery. The cathode and anode are graphite sheets of 0.2–1.5 mm and 0.4 mm galvanized plate (SGCC Z-C-X-Z18: JFE Galvanizing & Coating Co., Ltd.) with a zinc layer of about 18 µm, respectively. This thickness of the zinc layer for the anode active material corresponded to the theoretical electricity of 10 mAh/cm² which is a much higher than that of the active material for the cathode. The cathode side current collector is a galvanized plate, which is the same as the anode to provide mechanical strength. The electrolyte is a 10% sodium chloride water solution absorbed in the filter paper of 0.7 mm thickness. The standard size for the cell is 25 cm². Some properties of the primary battery, such as discharge energy, voltage and internal resistance, were measured.

3. Results and Discussion

3.1 Structure of graphite sheets

We investigated the structure of the graphite sheets. Figure 4 shows the XRD pattern of the graphite sheets with densities of 0.4–
1.6 g/cm³. The strong 002 peak for graphite was obtained from all the samples. The peak intensity increased with the increasing density. It was found from the XRD that the graphite sheets have a c-axis oriented structure and a graphene layer parallel to the surface of the graphite sheet. Figure 5 shows the surface morphology and cross section of the graphite sheets measured by FESEM and SPM. There were many very smooth areas of 100–1000 nm order on the surface. We thought that these were graphene layers because the strong 002 peak for graphite was obtained from all the samples by XRD. It was found from the cross section that 200–500 nm graphite layers were observed. The cross section of the graphite sheet have many µm-length order gaps which could work as air passages for the cathode of the metal air batteries. We think that oxygen as the active material for the cathode of the air metal battery can be obtained from the side edge of the graphite sheet.

3.2 Some properties of the graphite sheets

We investigated the gas permeation rate in the surface direction of the graphite sheet. Figures 6 and 7 show the relationship between the bulk density and thickness of the graphite sheet and gas permeation rate, respectively. The gas permeation rate increased

![Figure 4. XRD pattern of expanded natural graphite sheet having various densities of 0.4–1.6 g/cm³.](image)

![Figure 5. Surface morphology and cross section of the expanded natural graphite sheets measured by FESEM and SPM.](image)

![Figure 6. Relationship between bulk density of graphite sheet and gas permeation rate for the graphite thickness of 0.4 mm.](image)

![Figure 7. Relationship between thickness of graphite sheet and gas permeation rate for the bulk density of 1.0 g/cm³.](image)
with the decreasing bulk density and increasing thickness. The gas permeation rate of $1.0 \times 10^{-4}$ Pam$^{-1}$s$^{-1}$ corresponds to the amount of oxygen transferred at $4.0 \times 10^{-8}$ mol/sec. We measured the electric resistance in the thickness direction of the graphite sheet. Figure 8 shows the relationship between the bulk density and electric resistance for a thickness of 0.4 mm. The electric resistance decreased with the decreasing bulk density because the orientation of the graphene layer decreases with the decreasing bulk density of the graphite sheet and many graphene layers contact each other. These values are sufficient to use the graphite sheet as an electric collector for a battery.

3.3 Discharge properties

We investigated the relationships between the thickness and density of the graphite sheets and discharge energy. The discharge energy was calculated by multiplying the discharge capacity by the voltage. The thickness of these cells was 1.7–3.0 mm (graphite sheet: 0.2–1.5 mm, galvanized plate: 0.4 mm, filter paper: 0.7 mm). Figure 9 shows the influence of the thickness and density of the graphite sheets on the discharge energy at a 2.0 mA discharge current for a 5 cm $\times$ 5 cm cell size. The discharge energy increased with the decreasing thickness and decreasing density of the graphite sheets. We think that the reason why the higher the discharge energy for the smaller graphite sheet thickness is because the electric resistance is low, and the reason why the higher the discharge energy at the lower density of the graphite sheets is because the electric resistance is low and the gas permeation rate is high. The discharge current density of these experiments was 0.08 mA/cm$^2$ and the C rate was about 0.05 C for the battery using the standard graphite sheet as the cathode. It is well known that the cathode reaction for the metal air battery with a carbon cathode is a 2-electron reduction. Thus, the current calculated from the gas permeation rate of $1.0 \times 10^{-4}$ Pam$^{-1}$s$^{-1}$ corresponds to 7.7 mA at 300 K. Since the discharge current of 2 mA could be applied, it was suggested that the graphite sheet exhibited gas transport characteristics similar to those obtained in the permeation rate test even in the cell. This discharge current is not the rate-determining supply when considering the gas permeability of oxygen and thickness of the zinc layer on the galvanized plate.

The maximum discharge energy is at the density of 0.5 g/cm$^3$, because the graphite sheet having a density of less than 0.5 g/cm$^3$ could not be stably obtained. So, the graphite sheet with a thickness of less than 0.8 mm at the density of 0.5 g/cm$^3$ cannot be obtained. The graphite sheet having good properties for use as a cathode cannot be obtained in the red dot line triangle area in Fig. 9. In these experiments, the thickness and the density of the optimized graphite sheets are 0.8 mm and 0.5 g/cm$^3$, respectively. However, we need to develop the preparation methods for various graphite sheets with any thickness and density in order to improve the discharge energy of our battery in the future.

Figure 10 shows the discharge characteristics of metal air batteries using standard and optimized graphite sheets as the cathodes. The standard graphite sheet is used for the mass production of gaskets. Its thickness and density is 0.4 mm and 1.0 g/cm$^2$, respectively. The optimized graphite sheet for the metal air battery has the thickness of 0.8 mm and density of 0.5 g/cm$^3$. The discharge capacity increased to 3.2 mAh/cm$^2$ from 2.1 mAh/cm$^2$ by using the optimized graphite sheet. The discharge energy per battery volume increased from 5 mWh/cm$^3$ to 8 mWh/cm$^3$ using the optimized graphite sheet because the thickness of the optimized and standard cell are 1.9 mm (graphite sheet: 0.4 mm, galvanized plate: 0.4 mm $\times$ 2, filter paper: 0.7 mm) and 2.3 mm (graphite sheet: 0.8 mm, galvanized plate: 0.4 mm $\times$ 2, filter paper: 0.7 mm), respectively. The discharge energy for the optimized cell is about 1.5 times that of commercial products for the emergency metal air battery from FURUKAWA Co., Ltd. (Mag. BOX).

3.4 Battery connections

We studied the series connection for metal air batteries using our original sandwich structure shown in Fig. 3(B). This cell can use the oxygen as the active material from the side of the graphite sheets.
We think that oxygen gas as the active material for the metal air battery cannot be used in a cell size of more than 400 cm². We found from this result that our original sandwich structure for the cathode cannot move from the cross section in the large cell sizes of more than 400 cm².

The DC voltage proportionally and theoretically increase by increasing with battery cells independent of the thickness and density of the graphite sheets. The DC 12 V output can be obtained using 15 cells with the graphite sheets. We found that a metal air battery with our original structure is working well. This battery can be used in many applications, such as a backup power supply, emergency battery, etc., because of having a DC 12 V output.

We studied the parallel connection for metal air batteries using our original sandwich structure. Figure 11 shows the dependence of the discharge capacity of the metal air batteries on the cell size. The graphite sheet is for mass production with thickness of 0.4 mm and density of 1.0 g/cm³. The discharge capacity increase with the increasing cell size up to 400 cm² (20 cm × 20 cm). However, the discharge capacity is constant for a cell size of more than 400 cm². It was found from this result that our original sandwich structure for the metal air battery cannot be used in a cell size of more than 400 cm². We think that oxygen gas as the active material for the cathode cannot move from the cross section in the large cell sizes of more than 400 cm².

Figure 12 shows the relationships between the cell size and internal resistance. The graphite sheet is for mass production with thickness of 0.4 mm and density of 1.0 g/cm³. The internal resistance decreased with the increasing cell size. However, the internal resistance was about 2 ohms for the cell size of 150 cm² and maximized for a cell size of more than 150 cm². This internal resistance value is greater than other batteries such as the lithium ion battery and lead acid battery.

The DC resistance decreased with the increasing cell size. However, the DC resistance value is greater than other batteries such as the lithium ion battery and lead acid battery.

Discharge capacity/mAh

Cell size/cm²

Figure 11. Discharge capacity of the metal air batteries dependence on cell size.

Electric resistance/Ω

Cell size/cm²

Figure 12. Relationships between the electric resistance and cell size.

3.5 Applications
We think that this battery can be used in many applications, such as a backup power supply, emergency battery, etc., because a DC 12 V output can be obtained using 15 cells connected in series. Figure 13 shows a light-emitting diode (A) and smart phone charging (B) by our metal air battery having the original series connection structure. We confirmed that a light-emitting diode and smart phone charging by a metal air battery having the original series connection structure is possible.

The main parts of this battery are an expanded natural graphite sheet for the cathode, galvanized plate for the anode and electrolyte. The graphite sheet and galvanized plate are very cheap and have a good physical and chemical stability. These materials can be kept for a long time without a particular environment. We only need to prepare the electrolyte to activate this battery for an emergency. We think that this battery can be easily used in an emergency, if all battery parts, except for the electrolyte, can be stored in the disaster prevention compartment.

4. Conclusions
We studied the metal air battery using a graphite sheet as the cathode. The discharge energy of the metal air battery could be 8 mWh/cm² when the thickness and density of the graphite sheets are 0.8 mm and 0.5 g/cm³, respectively. This energy is about 1.5 times higher than that of commercial products (Mag. BOX). This battery can be used in many applications, such as a backup power supply, emergency battery, etc., because a DC 12 V output can be obtained using 15 cells connected in series.

Figure 13. Light-emitting diode (A) and smart phone (B) charging by our metal air battery having the original series connection structure.

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