Electrochemical Properties of Large-Discharge-Capacity Air Electrodes with Nickel Foam Sheet Support for Lithium Air Secondary Batteries

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ABSTRACT

Air electrodes with millimeter-order thickness for lithium air secondary batteries were prepared by loading electrode materials containing carbon and electrocatalyst into a single-layer nickel foam sheet or stacking three nickel-foam sheets loaded with the electrode materials. Discharge properties of the lithium air secondary battery cells incorporating these air electrodes were examined in 1 mol/l LiTFS/TEGDME under a pure oxygen flow. The cell incorporating the air electrode with carbon loaded into the three-layer stack of nickel-foam sheets with total thickness of 3 mm showed a rather large discharge capacity of about 80 mAh/cm² compared to about 30 mAh/cm² for the cell with a carbon-only air electrode incorporating a single nickel-foam sheet with 3-mm thickness. The cell incorporating an air electrode loaded with Pt₁₀Ru₉₀ electrocatalyst could be cycled under the condition of large cut-off capacities of 10 mAh/cm² at current density of 0.2 mA/cm².

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Keywords : Lithium Air Secondary Battery, Air Electrode, Nickel Foam Sheet, Electrocatalyst

1. Introduction

Lithium air secondary batteries (LABs) have been attracting attention because they show the highest theoretical energy density of about 3500 Wh/kg-Li₂O₂ based on the total cell reaction:

LABs are expected to be among the next generation of secondary batteries utilized as power sources for mobile tools such as smart phones and electric vehicles. However, many technical issues concerning battery performance remain. Since the first report by K. M. Abraham,¹ much research has sought to improve it, focusing mainly on the poor discharge/charge cycle properties. The poor cycle properties result from large overpotentials for the oxygen reduction reaction (discharge) and oxygen evolution reaction (charge) on the air electrode. Additionally, the inadequate stability of the nonaqueous electrolyte solutions due to oxygen radicals lead to a gradual decrease in discharge capacities during discharge/charge cycles. Therefore, much work has investigated the air-electrode materials, including the electrocatalyst,^{1–17} and the electrolyte solutions,^{1,17–26} from the viewpoint of improving the battery cycle performance.

The various kinds of air-electrode materials that have been examined to decrease the large overpotentials for both the electrode reaction of oxygen reduction/evolution include materials with high surface area or porous carbon materials^{2,3} and highly active electrocatalysts, such as metal phthalocyanine,^{1,4} noble metal alloys (Pt, Ru, Pd and Pt–Ru),^{5–8,10,17} single metal oxides (MnO₂, Co₃O₄, RuO₂)^{5–14} and Fe-, Mn-, and Co-based perovskite-type complexed oxides.^{15,16} Recently, we have investigated the electrocatalytic activities of Pt_{100–x}Ru_x (0 ≤ x ≤ 100) for air electrodes.⁸ Among these Pt–Ru electrocatalysts, nanometer-scale Pt₁₀Ru₉₀ particles that had been homogeneously dispersed over the KB resulted in superior cycle performances.⁸ Moreover, electrolyte solutions, such as dimethyl sulfoxide (DMSO)^{17–21} and tetraethylene glycol dimethyl ether (TEGDME),^{22–24} and ionic liquids,^{25,26} have been shown to be stable solutions under LAB operating conditions.

Most previous research was simply conducted by evaluating the gravimetric discharge/charge capacity (per electrode weight) as the principal index. Some papers^{23,27} have reported very large gravimetric discharge capacities of 5,000–10,000 mAh/g-carbon even though the areal loading of air-electrode material was less than 1 mg/cm². Actually, these gravimetric values correspond to rather small areal capacity of less than 2–3 mAh/cm²,^{28–35} comparable to that of conventional lithium ion batteries. This low loading might result in the low energy density of practical LAB cells. Thus, to be more exact, evaluating by gravimetric values is not desirable because the active material for the positive air electrode is gaseous oxygen, whose quantity is difficult to measure. Furthermore, it is necessary to evaluate areal discharge/charge capacities to increase practical battery energy density. Recently, some trials^{36–38} have been reported with a similar view. Y. Lin et al. reported holey-graphene-based air electrodes with high loading of up to 10 mg/cm².³⁸ The LAB cell with an ultrathick air electrode exhibited rather large discharge capacity of about 40 mAh/cm². On the other hand, A. Nomura reported a loading of 10 mg/cm² in air electrodes composed of flexible carbon nanotube (CNT) sheets sandwiched between two gas-diffusion layers.³⁷ This unique flexible structure enables a large amount of discharge product Li₂O₂ and thus leads to large discharge capacity of about 30 mAh/cm².

Thus, some approaches for improving areal capacities have focused on developing air-electrode material with unique structures, such as CNTs and graphene. Geometric factors such as air-electrode thickness should have an influence on the electrochemical properties of LAB cells. In these approaches, the air electrodes investigated had micrometer-order thickness. Experimental results on air electrodes with millimeter-order thickness are lacking due to difficulty in preparing such a thick air electrode by the conventional process of coating a slurry solution of electrode materials on a carbon sheet or carbon paper. Actually, air electrodes of millimeter-order thickness are too thick from the practical point of view. However, the dependence of the electrochemical properties of LAB on air-electrode thickness ranging from micrometer to millimeter order should be investigated to improve their areal discharge

capacities. In this study, nickel foam sheets with various thicknesses were used as support material to fill them with electrode materials of carbon powder and electrocatalyst powder. The air-electrode thickness can be controlled by using nickel foam sheets with various thicknesses. A nickel foam sheet has already been used as support material for the air electrode elsewhere,³⁹ but the electrochemical properties, such as the dependence of cycle performance on air-electrode thickness, were not discussed extensively. Actually, use of heavy nickel foams diminishes practical gravimetric energy densities of the LABs. However, various knowledge on using the nickel foams as the air-electrode material would apply to more lightweight foam material such as carbon. The objective of this study was to figure out a design principle for thick air electrodes with millimeter-order range thickness with large areal discharge capacity to contribute to the realization of high-energy-density LABs.

2. Experimental

2.1 Synthesis of electrocatalyst, Pt₁₀Ru₉₀/carbon

Pt₁₀Ru₉₀/KetjenBlack EC600JD carbon (KB, Lion Co.) was prepared by the formic acid reduction method.⁸ The ratio of Pt₁₀Ru₉₀ to KB powder was adjusted to 1:8 by weight. The KB powder was immersed in formic acid solution by ultrasonic treatment. A mixed solution of H₂PtCl₆·6H₂O (Kanto Chemical Co.) and RuCl₃ (Furuya Metal Co., Ltd.) was dropped into the suspension of KB powder and the formic acid solution, which was then stirred overnight. The Pt–Ru/KB powder was collected from the suspension by evaporation to dryness at 50°C. Finally, Pt₁₀Ru₉₀/KB powder was dried by heat-treating the mixture at 300°C for 12 h in Ar.

2.2 Preparation of air electrodes with nickel foam sheet support loaded with KB only or Pt₁₀Ru₉₀/KB

First, one slurry was prepared by mixing Pt₁₀Ru₉₀/KB powder and PVdF (Kureha Battery Materials Japan Co.) binder in N-methyl-2-pyrrolidone solvent (Tomiya Pure Chemicals Industries Ltd.). Another was prepared without Pt₁₀Ru₉₀ electrocatalyst by using as-received KB powder. The resultant composition in the air electrode was adjusted to be Pt₁₀Ru₉₀:KB:PVdF = 10:80:10 or KB:PVdF = 90:10 in weight.

Millimeter-order-thick air electrodes with two kinds of stacking structures were prepared using nickel foam sheets. Nickel foam sheets with 95% voids and thickness of 0.6, 1, and 3 mm were purchased from Magnex Co., Ltd. Single-layer air electrodes with a nickel foam sheet support (thickness of 0.6, 1, and 3 mm; diameter of 16 mm) were prepared by homogeneously coating the slurry suspension on both sides of the sheet with a spatula and drying the sheet loaded with the slurry at 80°C for 12 h and at 100°C for 12 h in vacuo. Multi-layer air electrodes were prepared by stacking more than one undried nickel foam sheet loaded with the slurry in a concentric pattern and then drying the stack under the same condition as above. The multilayer air electrodes were confirmed to be of adequate strength. The amounts of Pt₁₀Ru₉₀, KB, and PVdF to load into the sheet were calculated from weight changes before and after the drying process. The packing state of electrode materials in the voids of the sheet was observed with a scanning electron microscope (SEM) (Carl Zeiss, Inc., ULTRA55) and by energy dispersive X-ray spectroscopy (Bruker Corp., Quantax).

2.3 LAB cell assembly and electrochemical measurements

Commercially available ECC-Air cells (EL-Cell GmbH) were used as the LAB cells. The air electrode, an electrolyte solution of 1 mol/l lithium bis(trifluoromethanesulfonyl) amide [LiTfSA]/tetraethylene glycol dimethyl ether [TEGDME] (Tomiya Pure Chemicals Industries Ltd.), a glass separator (EL-Cell GmbH), and lithium metal sheet (thickness: 600 µm, Honjo Metal Co., Ltd.) were

installed in the LAB cells. Electrochemical measurements were carried out with a discharge-charge measurement system (Hokuto HJ1001SD8) under a galvanostatic condition of 0.2 mA/cm² in a pure oxygen flow. The discharge and charge capacities were normalized by the geometric surface area (2 cm²) of the air electrode. Cycle tests were conducted under conditions of limited discharge/charge with a cut-off capacity of 10 mAh/cm² in a voltage range of 2.0 V(discharge)–4.2 V(charge). To analyze the discharged air electrodes, the LAB cells were opened after the discharge process, and the electrodes were washed with dimethyl carbonate and dried in a vacuum atmosphere. The formation phase of the discharge product was identified with a powder X-ray diffractometer (XRD) (Rigaku Co., X-ray diffractometer Ultima IV) using CuK_α radiation. The morphology of the discharge product deposited on the air electrode was observed with the SEM.

3. Results and Discussion

3.1 Discharge properties of single-layer air electrode with one nickel foam sheet

The single-layer air electrodes were prepared by using a nickel foam sheet with thickness of 0.6, 1, and 3 mm loaded with only KB carbon to examine the dependence of the electrochemical properties on air-electrode thickness. The amounts of KB and PVdF loaded into the nickel foam were 3.9, 8.8, and 17 mg/cm² for the nickel-foam thickness of 0.6, 1, and 3 mm, respectively. In addition, the electrode materials were completely packed inside the nickel foam sheet. Therefore, the thickness of the nickel foam sheet was regarded as the thickness of the air electrode. The loading of 17 mg/cm² was notably high even though the air-electrode in this study was much thicker than the ones in previous reports focusing on the areal capacities,^{36–38} which indicated the use of a nickel foam sheet was effective for obtaining high-loading air electrodes. Figure 1 shows discharge curves of LAB cells incorporating air electrodes prepared thus. All of the cells exhibited rather large discharge capacities of 31 mAh/cm² for air-electrode thickness of 3 mm, and obviously they also have plateau voltages of 2.5–2.7 V, which are very similar to the typical discharge curves for LAB cells reported so far. These results indicate the effectiveness of using a nickel foam sheet as support material for air electrodes and of the method to load the electrode materials into the sheet. As shown in Fig. 1, the cell exhibited larger discharge capacities as the air-electrode thickness increased. This behavior suggests that the reaction sites for oxygen reduction increased by loading larger amounts of carbon materials into the sheet. As a result, the areal discharge capacities of the air

Figure 1. Discharge curves of LAB cells incorporating air electrodes with single-layer nickel foam sheet of (i) 0.6, (ii) 1, and (iii) 3 mm in 1 mol/l LiTfSA/TEGDME under the galvanostatic condition of 0.2 mA/cm². Air electrode composition: KB:PVdF = 9:1. Loading: (i) 3.9 mg/cm², (ii) 8.8 mg/cm², and (iii) 17 mg/cm².

Figure 2. (a) Cross-sectional SEM image and (b) EDS mapping profile of carbon in as-prepared air electrode with 3-mm single-layer nickel foam sheet loaded with KB and PVdF. (i) KB and PVdF, (ii) nickel foam, and (iii) KB (red mapping).

electrode have a proportional relationship with the air-electrode thickness. However, the discharge capacities show less complete linear proportion with the thickness. For example, although the cell with air-electrode thickness of 0.6 mm showed the capacity of 19 mAh/cm², the cell with the thickness of 3 mm showed a value of 31 mAh/cm², much smaller than expected. These unexpected results would be due to the different packing density of electrode materials in each nickel foam sheet.

Figure 2 shows a cross-sectional SEM image and an EDS mapping profile of an as-prepared air electrode with a 3-mm thick single-layer nickel foam sheet loaded with KB and PVdF. Red areas indicate the presence of carbon in the EDS profile. The SEM image reveals that the carbon materials are loaded into both faces even though they are scarcely loaded into the central region, as shown in Fig. 2(a). This tendency agrees well with the EDS result, where red areas indicating the presence of carbon are not seen in the central region, as shown in Fig. 2(b). These results suggest that the method of loading carbon slurry into the foam materials could not uniformly fill nickel foam as thick as 3 mm with carbon materials. Such an inhomogeneous filling state would lead to an imperfect direct proportion of the areal discharge capacity to the electrode thickness and nonconstant gravimetric/volumetric discharge capacity (see Fig. S1).

3.2 Discharge properties of air electrodes with multi-layer nickel foam sheet

Figure 3 shows discharge curves of LAB cells incorporating air electrodes with a three and four-layer nickel foam sheets with 1-mm thickness (hereafter referred to as 1 mm × 3 and 1 mm × 4). The curve for the LAB cell with a single-layer Ni-foam sheet of 3 mm is included for comparison. The amounts of KB and PVdF loaded into the nickel foam were 22 and 23 mg/cm² for 1 mm × 3 and 1 mm × 4 nickel foam sheets, respectively. These values are very high compared to the ones for the single-layer nickel foam sheets. Stacking nickel foam sheets is a suitable way to increase the areal loading as high as 20 mg/cm². Both air electrodes showed almost the same loading even though the number of stacked sheets was different. This suggests that the slurry containing electrode materials might not be retained in the thicker nickel foam in the slurry-filling process, and, moreover, the electrode materials might drip from the nickel-foam sheet in the drying process. This issue might be overcome by optimizing the voids in the nickel foam sheet. The LAB cell with nickel foam support of 1 mm × 3 exhibited a rather

Figure 3. Discharge curves of LAB cells incorporating air electrodes with multilayer nickel foam sheet of (i) 1 mm × 3 and (ii) 1 mm × 4 in 1 mol/l LiTFS/TEGDME under the galvanostatic condition of 0.2 mA/cm². (iii) The curves in using a single-layer sheet of 3 mm for comparison. Air electrode composition: KB:PVdF = 9:1.

Figure 4. Cross-sectional SEM images of air electrodes with (a) single-layer nickel sheet of 1 mm and (b) multilayer nickel foam sheet of 1 mm × 3. Both electrodes were loaded with KB and PVdF. (a) KB and PVdF, (b) nickel foam. The dotted lines in image (b) show the layer boundaries. (i) KB and PVdF, (ii) nickel foam.

large discharge capacity of 83 mAh/cm² and a plateau voltage of 2.6 V, indicating the effectiveness of multilayer nickel-foam support for the air electrode. The cell with the nickel foam support of 1 mm × 4 exhibited a smaller discharge capacity than the one for 1 mm × 3; however, the former cell should exhibit larger discharge capacity than the latter one. This behavior reflects the fact that the loading was almost the same for both air electrodes. Moreover, the longer diffusion path of O₂ in the thicker air electrode might inhibit the formation of a triple phase boundary as the reaction site for oxygen reduction. On the other hand, clearly the LAB cell with nickel foam sheets of 1 mm × 3 exhibited larger discharge capacity than the one with 3 mm × 1, though both electrodes had the same total thickness of 3 mm. This suggests that there is a distinct difference in the internal structure of these two air electrodes.

SEM observation was carried out to clarify the internal structure of the air electrodes with the multilayer nickel foam sheet regarding the discharge properties shown in Fig. 3. Figure 4 shows cross-sectional SEM images of air electrodes with a multilayer nickel sheet of 1 mm × 3 and a single-layer nickel sheet of 1 mm × 1. KB and PVdF densely filled the nickel foam sheet of 1 mm × 1 as

Figure 5. SEM images and photographs of air electrodes with nickel foam sheet of 1 mm × 3 (a) before and (b) after discharge test as shown in Fig. 3, curve (i).

shown in Fig. 4(a). On the other hand, more electrode material was filled into each nickel foam sheet in the multilayer stack of 1 mm × 3, but there were some voids in the boundary region between each foam sheet. The loading of 23 mg/cm² for the multilayer sheet of 1 mm × 3 is evidently higher than 17 mg/cm² for the single-layer sheet of 3 mm × 1. Thus, the procedure for stacking a number of nickel foam sheets is suitable for densely filling them with electrode materials for air electrodes of over 1 mm. Such high-density filling of electrode materials would have a great effect in achieving the rather large capacity of 83 mAh/cm² shown in Fig. 3. These results indicate that the key to obtaining large areal capacity is to control the internal structure of the air electrode.

3.3 Analysis of discharge reaction over air electrodes with nickel foam sheet

The morphological characteristics and formation phase of discharge products were analyzed to investigate the electrochemical reaction on the air electrodes tested in this study. Figure 5 shows SEM images of air electrodes with a nickel foam sheet of 1 mm × 3 before (as prepared) and after the discharge test shown in Fig. 3(i), together with overview photographs of as-prepared and discharged air electrodes. The observation of the discharged air electrode was carried out at the one side of the electrode in contact with the electrolyte solution. From the SEM images, the as-prepared air electrode was composed of a large number of KB primary particles with a diameter of about 30 nm. After discharging, the primary particles became larger by 100 nm in diameter and more thickly combined with each other. This particle growth occurred as a result of the deposition of discharge products in the same manner as reported in our previous study.² On the other hand, there were no notable shape changes between as-prepared and discharged air electrodes as indicated in the photographs of Fig. 5. This result suggests that some voids in the air electrode would absorb the

Figure 6. XRD pattern of air electrodes with nickel foam sheet of 1 mm × 3 after discharge test as shown in Fig. 4, curve (i). (a) Wide range (20–80 deg), (b) narrow range (30–40 deg).

volume expansion that occurred due to deposition of the discharge product or that the robust structure of nickel foam would inhibit the shape change of the air electrode during the discharge process.

The formation phase deposited on the discharged electrode was identified by ex situ XRD measurement. Figure 6 shows the XRD pattern of the discharged air electrode in Fig. 5(b). There are sharp peaks identified as Ni and NiO derived from the nickel foam as shown in the wide-range pattern of Fig. 6(a). A broad pattern corresponding to amorphous carbon (KB) was also observed around 20 degrees. No peaks corresponding to by-product such as Li₂CO₃ were confirmed in this pattern. There are some broad peaks around 33, 35, 40, 50 and 59 degrees as shown in Fig. 6(a). These broad peaks indicate a low degree of crystallization of discharge products. The narrow-range pattern from 30 to 40 degrees is shown in Fig. 6(b) to investigate these broad peaks. These broad peaks except 50 degrees were identified as Li₂O₂ (PDF No. 01-073-1640) as shown in Fig. 6(a) and (b). These results reveal that the oxygen reduction reaction making use of oxygen as a positive active material proceeded on the air electrode and produced discharge product Li₂O₂.

3.4 Discharge/charge properties of air electrodes with multilayer nickel foam sheet

The LAB cell incorporating an air electrode with a multilayer nickel foam sheet of 1 mm × 3 exhibited the largest discharge capacity of about 80 mAh/cm² among the cells. Air-electrode electrocatalysts, such as metal oxides and noble metal alloys, are

well known to enhance electrochemical activities for oxygen reduction/oxygen evolution reactions. Most of the LAB cells with an air electrode composed of carbon and binder without an electrocatalyst have exhibited poor cycle performance.^{3,5,7,13,15,27,29} Here, $\text{Pt}_{10}\text{Ru}_{90}/\text{KB}$ electrocatalyst, as reported in our previous paper,⁸ was used to improve the cycle properties. In that paper, the air electrode with micrometer-order thickness was prepared by coating $\text{Pt}_{10}\text{Ru}_{90}/\text{KB}$ on the Ti mesh. The LAB cell with the air electrode exhibited comparatively stable cycle properties of over 800 mAh/g at the 8th cycle under the condition of cut-off capacity of 1000 mAh/g at 0.1 mA/cm². The XRD patterns of the air electrodes showed reversible deposition/decomposition of Li_2O_2 in a low degree of crystallization as the discharge product at the first cycle. The effectiveness of $\text{Pt}_{10}\text{Ru}_{90}/\text{KB}$ electrocatalyst for the millimeter-range-thickness air electrode was evaluated by measuring discharge/charge properties of the cells with the multilayer sheet of 1 mm × 3 with/without the electrocatalyst. Figure 7 shows discharge/charge curves and cycle properties of LAB cells incorporating air electrodes with a multilayer nickel foam sheet of 1 mm × 3 under the condition of cut-off capacity of 10 mAh/cm² at 0.2 mA/cm². The electrochemical properties of air electrodes with/without $\text{Pt}_{10}\text{Ru}_{90}$ loading were examined to investigate the electrocatalysis of $\text{Pt}_{10}\text{Ru}_{90}$. Both LAB cells showed similar discharge curves, and the cell with $\text{Pt}_{10}\text{Ru}_{90}$ showed a certain decrease in charge voltage at the 1st cycle as shown by the first curves in Fig. 7(a). The cell with $\text{Pt}_{10}\text{Ru}_{90}$ showed a smaller increase in discharge/charge overpotentials than the unloaded cell after 25 cycles. This result indicates that the Pt–Ru electrocatalyst could enhance the cycle stability. As shown in Fig. 7(b), both cells showed constant discharge capacities of 10 mAh/cm²; however, there were irreversible capacities in the cell without $\text{Pt}_{10}\text{Ru}_{90}$. The charge capacities for the cell without $\text{Pt}_{10}\text{Ru}_{90}$ drastically decreased after the 15th cycle due to the larger overpotential for the charge reaction. The discharge products were completely decomposed on the air electrode without $\text{Pt}_{10}\text{Ru}_{90}$ in the charge process, and this led to poor cycle properties. These results suggest that $\text{Pt}_{10}\text{Ru}_{90}$ electrocatalyst would enhance the reversibility in the electrochemical reactions of oxygen reduction/evolution.

The cycle properties under the conditions of large cut-off capacity of about 50 mAh/cm² and high current density of 1.0 mA/cm² are shown in Fig. S2 and Fig. S3 of Supporting Information, respectively. These figures indicate that LAB cells with a multilayer nickel foam sheet can work under the cycle conditions of large cut-off capacity and high current density, even though noticeable performance degradation was confirmed during the cycle tests.

The above cycle-test results indicate that the $\text{Pt}_{10}\text{Ru}_{90}$ had electrocatalytic activities for improving the electrochemical properties of LAB cells with an air electrode of a wide range of thickness from micrometers to millimeters. However, the formation phase of discharge product could not be identified as Li_2O_2 for all the air electrodes with $\text{Pt}_{10}\text{Ru}_{90}$ (Fig. 7, Fig. S2, and Fig. S3), which suggests that the discharge product was not crystalline but amorphous. The low-crystallinity Li_2O_2 as the discharge product was confirmed for both the electrode of millimeter-order thickness without electrocatalyst (Fig. 6) and the air electrode of micrometer-order thickness with $\text{Pt}_{10}\text{Ru}_{90}$ electrocatalyst shown in previous report.⁸ Moreover, crystalline Li_2O_2 was difficult to confirm when using RuO_2 as electrocatalyst for air electrode in TEGDME-based electrolyte solution as reported elsewhere.⁴⁰ These results suggest that the Ru-based electrocatalyst led to amorphization of discharge product Li_2O_2 as a result of catalyst properties of the Ru-based compound. Such amorphization was also provoked by difficulty in the diffusion of oxygen in millimeter-order thick air electrode. The crystallinity of the discharge product Li_2O_2 is an important factor for improving the cycle properties. Therefore, it is necessary to control

Figure 7. (a) Discharge/charge curves and (b) cycle properties of LAB cell incorporating air electrodes with multilayer nickel foam sheet of 1 mm × 3 in 1 mol/l LiTfSA/TEGDME under the condition of cut-off capacity of 10 mAh/cm² at 0.2 mA/cm². Air electrode composition: (i), $\text{Pt}_{10}\text{Ru}_{90}:\text{KB}:\text{PVdF} = 10:80:10$ and (ii) $\text{KB}:\text{PVdF} = 90:10$.

its crystallinity by further optimizing the component materials and structures of air electrodes.

4. Conclusions

Air electrodes with millimeter-order thickness were fabricated to increase the areal discharge capacities by loading electrode material such as carbon and electrocatalyst into nickel foam sheet support. Electrochemical properties of LAB cells with a nickel foam support with various thicknesses were investigated to clarify their correlation with the internal structures of air electrodes. The findings obtained are summarized below.

- (1) A LAB cell incorporating the single-layer air electrode with 3-mm thickness showed large capacity of about 30 mAh/cm².
- (2) A LAB cell incorporating a multilayer air electrode with total thickness of 3 mm showed much larger discharge capacity of about 80 mAh/cm² even though the thickness was the same as that of the single-layer air electrode.
- (3) SEM observation revealed that electrode materials were more densely loaded in the multilayer electrode than in the single-

layer one in the case of the same electrode thickness. This loading state of electrode materials results in the large difference in the discharge capacities.

- (4) The LAB cell with multilayer air electrode showed stable discharge capacity of 10 mAh/cm² after 30 cycles under the condition of cut-off capacity of 10 mAh/cm², indicating effectiveness of Pt–Ru electrocatalyst on improvement in the cycle properties.

Supporting Information

The Supporting Information is available on the website at DOI: <https://doi.org/10.5796/electrochemistry.18-00045>.

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