



Short communication

Li metal utilization in lithium air rechargeable batteries

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HIGHLIGHTS

- Reducing the Li metal amount will offer anode effects on the performance.
- Realization of theoretical specific energy density was confirmed on Li-air batteries.
- Low cycle stability was attribute to Li dendrite formation during cycle.

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ABSTRACT

Effects of Li amount used for anode on the discharge capacitance of a lithium-air battery were studied in order to investigate the effects of Li usage. On the basis of Ketjenblack air electrode, electrochemical analysis were performed in the voltage range of 4.5–2.0 V. Because the amount of Li limits the overall discharge capacity, the capacity decreases with decreasing the Li amount in the cell. Although only 370 mAh g⁻¹ (gram of air electrode) of capacity was obtained by reducing the Li amount to 0.9 mg, almost 100% of Li can be used for discharge and it is corresponded to 4111 mAh g⁻¹ (gram of Li) with reasonable cycle stability. To confirm the residual amount of Li on anode, ICP measurement was performed after first discharge. Decrease in capacity with cycle number can be assigned to the decreased amount of Li dissolved and this could be related with formation of dendrite and porous Li deposition.

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1. Introduction

Recently, there has been sharply increased attention to lithium-air rechargeable batteries because of its high theoretical specific energy density, which is a desirable characteristic for high energy density requested for electric, hybrid, and plug-in hybrid vehicle. The theoretical specific energy density (excluding oxygen) is 11,140 Wh kg⁻¹, which is much higher than that of other advanced batteries [1]. The use of metallic lithium could make it possible to have high theoretical specific energy density value with very simple mechanism. During the discharge reactions, lithium ions dissolve into the electrolyte ($\text{Li} \rightarrow \text{Li}^+ + e^-$) from the Li metal anode, and oxygen reduction was occurred on air electrode. When oxygen reduction reaction is occurred, the processes are so complex depending on the type of electrolyte. Several recent papers have focused on the discharge chemistry and revealed that Li₂O₂ is

a principal product when stable electrolyte is used [2,3], however, in some case, Li₂O₂ is converted to Li₂CO₃ [4,5] resulting in low cycle stability. Further studies have been concentrated on the effects of catalyst to reduce the over-potential [3,6], high capacity, and lowering the charge potential [7,8]. Although large parts of studies on lithium-air battery are performed on air electrode or liquid electrolyte, usage of Li metal is another critical important issue in lithium-air batteries for realizing high energy density. However, in previous studies, researches about Li metal electrode are still not thoroughly studied, especially utilization of Li metal for discharge. Although importance of Li metal on the lithium-air battery system [2,9] is reported, number of research on the details of anode electrode was limited up to now. On the other hands, it is well known that dendrite forms on anode during charge for metal-air battery and this causes problems for cycle stability of metal-air rechargeable battery. Therefore, studies on change in morphology of anode are highly important for metal-air rechargeable battery. Therefore, in this study, we investigated the Li metal utilization to confirm whether all Li can be used for discharge when capacity of air electrode is large enough. This is simply done by increasing ratio of

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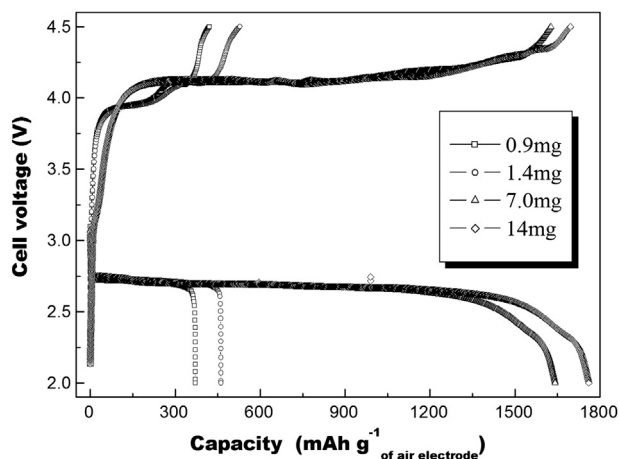


Fig. 1. Charge–discharge curves of lithium–air batteries using Ketjenblack based air electrode with various amounts of Li as an anode.

cathode to anode weight. Effects of surface morphology change of Li metal on cycle stability are also studied.

2. Experimental

Charge and discharge property of lithium–air batteries were measured by using Swagelok-type cells. The cathodes for the lithium–air batteries were prepared by casting a mixture of Ketjenblack (EC600JD, LION Co. Ltd), manganese oxide powder (EMD, Denka Co. Ltd.), and PTFE as a binder with a total ratio of 85:5:10. The electrode mixture was pressed onto a stainless steel mesh and the cathode was dried at 160 °C under vacuum oven for 5 h. Various amounts of Li foil (thickness: 0.1 mm, Shinjo Metallic Co. Ltd.) were used as the anode and separated by two pieces of glass fiber separator (Toyo Roshi Kaisha Ltd, ADVANTEC). The mixed solution of ethylene carbonate and diethyl carbonate (3:7 by volume) including lithium salts of 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was used as an electrolyte. All cells were gas-tight excepting for the stainless steel mesh windows to adopt 1 atm of oxygen gas. To verify Li remaining after the first discharging, ICP analysis was performed by PerkinElmer, Optima 5300DV for determining the change in Li usage. After first discharge, the cell was disassembled in a glove-box filled with Ar gas, and then anode

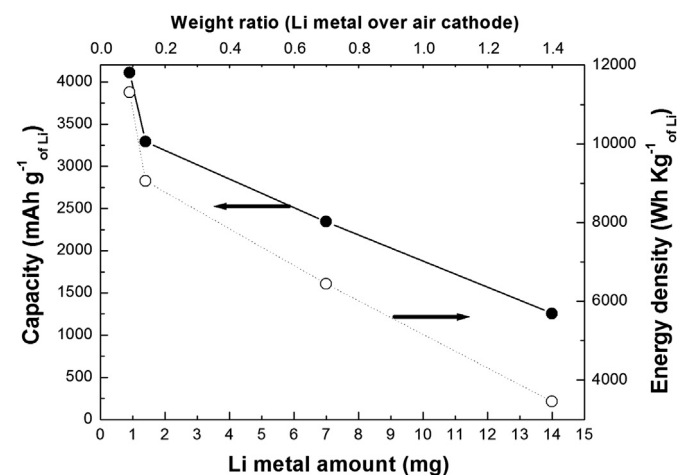


Fig. 2. Specific capacity and energy density as a function of Li amount in the lithium–air batteries using Ketjenblack air electrode.

Table 1

ICP analysis of anode using 0.9 mg of lithium after first discharge.

	Initial Li metal amount	Li metal remains
Volumetric amount	180 mg L ⁻¹	0.279 mg L ⁻¹
Practice amount on anode	0.9 mg	1.48×10^{-3} mg

mesh was washed in a PC solution to remove the Li effect from electrolyte. The dried mesh in the glove-box was dipped into water and then Li amount in water was measured with ICP.

3. Results and discussion

In order to investigate the Li amount effects on the discharge capacity of lithium–air batteries, various amounts of Li metal were used as the anode and Ketjenblack was used as the cathode electrode mixed with EMD and PTFE. It is also noted that the weight of cathode was always fixed 10 mg in this study. Electrochemical reaction between oxygen and lithium occurs on the surface of the carbon. Therefore, Ketjenblack was usually chosen for the air electrode material [7]. Fig. 1 shows the charge and discharge curve at initial cycle with different amount of Li for anode. In this figure, discharge and charge capacity were expressed by air electrode base. Unless otherwise noted, 14 mg of Li, which was pressed onto a stainless steel mesh, was used for a counter electrode of the lithium air battery. This cell was denoted as an ordinary cell in the following part. In case of discharge curves of samples, all cells show potential plateau at 2.75 V stably. The discharge capacity of 1760 mAh g⁻¹ (gram of air electrode), which is corresponded to ca. 33% of Li utilization, could be obtained in case of an ordinary cell. In order to obtain the specific

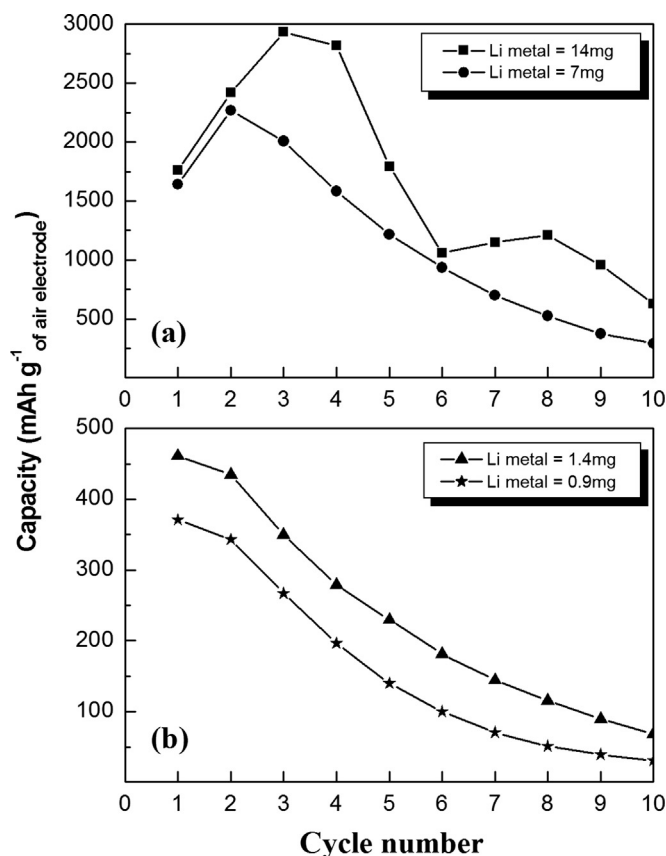


Fig. 3. Cycle retention rate of lithium–air batteries using Ketjenblack based air electrode with various amounts of Li. The amount of air electrode used is 10 mg.

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