



Controlling porosity of porous carbon cathode for lithium oxygen batteries: Influence of micro and meso porosity



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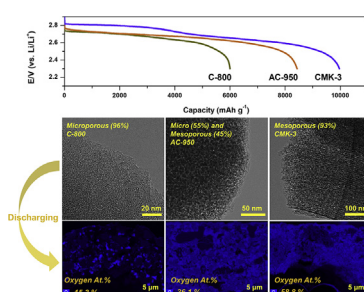
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HIGHLIGHTS

- Highly microporous, micro/meso porous, mesoporous carbon cathodes were prepared.
- The relationship between carbon porosity and cell performance was investigated.
- Discharge capacity of Li-O₂ cell was increased proportionally to the meso porosity.
- Microporous carbon cathode had great cycle stability than that of mesoporous carbon.
- The carbon porosity affected the morphology and quantity of discharge products.

GRAPHICAL ABSTRACT



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ABSTRACT

In rechargeable lithium-oxygen (Li-O₂) batteries, the porosity of porous carbon materials plays a crucial role in the electrochemical performance serving as oxygen diffusion path and Li ion transfer passage. However, the influence of optimization of porous carbon as an air electrode on cell electrochemical performance remains unclear. To understand the role of carbon porosity in Li-O₂ batteries, carbon materials featuring controlled pore sizes and porosity, including C-800 (nearly 96% microporous) and AC-950 (55:45 micro/meso porosity), are designed and synthesized by carbonization using a triazine-based covalent organic polymer (TCOP). We find that the microporous C-800 cathode allows 120 cycles with a limited capacity of 1000 mAh g⁻¹, about 2 and 10 times higher than that of mixed-porosity AC-950 and mesoporous CMK-3, respectively. Meanwhile, the specific discharge capacity of the C-800 electrode at 200 mA g⁻¹ is 6003 mAh g⁻¹, which is lower than that of the 8433 and 9960 mAh g⁻¹ when using AC-950 and CMK-3, respectively. This difference in the electrochemical performance of the porous carbon cathode with different porosity causes to the generation and decomposition of Li₂O₂ during the charge and discharge cycle, which affects oxygen diffusion and Li ion transfer.

1. Introduction

Rechargeable Li-O₂ batteries have attracted attention because their

theoretical gravimetric and volumetric energy densities (3600 Wh kg⁻¹ and 1000 Wh L⁻¹, respectively) are the highest among all known batteries [1–3]. Typical Li-O₂ batteries consist of a lithium metal anode,

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a carbon-based cathode, and an organic electrolyte in a cell [4–6]. Carbon materials have unique advantages, including low weight and cost and high specific surface area, porosity, and conductivity. For these reasons, they are able to achieve the desired specific energy densities required for practical Li-O₂ batteries and are therefore promising candidate materials for the cathode [7,8]. Researchers have studied various types of carbon materials to exploit these advantages, such as multiwall carbon nanotube (MWCNT), ketchen black (KB), hierarchically porous honeycomb-like carbon, porous carbon aerogels, and graphene [9–13]. These studies have attempted to understand how the air cathode structure affects electrochemical performance in Li-O₂ batteries. Some studies have reported a strong relationship between the surface area of the carbon materials and cell performance [14,15]. Others have demonstrated that the pore size and volume govern the performance of the Li-O₂ battery [16–18]. That is, the air cathode structures its porosity, surface area, and pore size played a critical role in the electrochemical performance of Li-O₂ batteries.

In particular, the various impacts of the pore size and distribution on mass transfer in porous carbon materials have been attributed to the limited ion conductivity and oxygen solubility and diffusivity in non-aqueous electrolytes [19–21]. Ding et al. investigated the influence of porous carbon cathodes in Li-O₂ batteries and showed that the capacity of the cell increased with the pore size [22]. Im et al. reported that the specific capacity was determined by the pore volume of carbon rather than its surface area and that a larger pore volume, which could accommodate more Li₂O₂, is preferable [23]. Thus, these studies have demonstrated that the porosity and pore size of the air electrode affect the performance of Li-O₂ batteries. If the microstructure of the air electrode could be controlled, the optimization of pore size and distribution in porous carbon could provide useful insights by improving our understanding of the quantitative relationship between the porosity of the carbon and the performance of the Li-O₂ battery. However, a systematic optimization of porous carbon as an air electrode has been not conducted experimentally owing to challenging experimental conditions.

In this work, we propose a correlation between the carbon pore size and the Li-O₂ battery performance by controlling the micro- and mesoporous structure of carbon materials. The microporous carbon is synthesized using a triazine-based covalent organic polymer (TCOP) with a regular microporous structure, followed by carbonization at 800 °C (C-800) in a nitrogen atmosphere. With the purpose of confirming the effect of porosity in the lithium oxygen battery system, mesoporous carbon is fabricated by a physical activation process at 950 °C with a carbon dioxide atmosphere (AC-950). In addition, ordered mesoporous carbon (CMK-3) with an approximately mesoporous structure was purchased from ACS Material, LLC (USA).

2. Experimental section

2.1. Materials

Cyanuric chloride, 1,3,5-triphenylbenzene, anhydrous aluminum chloride, dichloromethane (DCM), lithium nitrate, and polytetrafluoroethylene (PTFE, 60 wt.% dispersed in water) were supplied from Sigma Aldrich (USA). CMK-3 (ordered mesoporous carbon) was acquired from ACS Material, LLC. Dimethylacetamide and ethyl alcohol were purchased from Wako Chemical (Japan).

2.2. Synthesis of a triazine-based covalent organic polymer

Scheme 1 shows the fabrication procedure of microporous carbons and activated carbons derived from a triazine-based covalent organic polymer (TCOP). Preferentially, the triazine-based COP was synthesized by Friedel-Craft alkylation. In this case, a 250 mL round bottom flask was filled with DCM (100 mL) and cyanuric chloride (2.45 g, 8 mmol) and 1,3,5-triphenylbenzene (1.48 g, 8 mmol) were added. The mixture

was kept at 20 °C, and anhydrous aluminum chloride (3.00 g, 24 mmol) was added slowly. Then, the round bottom flask containing the reaction mixture was fitted with a condenser and refluxed for 16 h. When the reaction was complete, the resulting mixture was cooled to room temperature, and a brownish-black solid precipitate was collected by filtration. The crude powder was washed with DCM to remove unreacted precursor and both methanol and water were used repeatedly to eliminate residue. Finally, the brownish-black solid powder was dried in a vacuum oven for 24 h to obtain solvent-free material in an 85–90% yield.

2.3. Fabrication of porous carbon materials

To fabricate microporous carbon (C-800), synthesized TCOP was carbonized at 800 °C for 2 h under a nitrogen atmosphere in a tubular furnace. The physical activation process was conducted at 950 °C for 1 h under carbon dioxide to fabricate carbon with multiple pore structures (AC-950). The heating and gas flow rates were 5 °C/min and 100 mL/min, respectively. Finally, the carbonized and activated carbons were collected as dark powders.

2.4. Electrochemical measurement

The cathode electrodes composed of carbon and poly(tetrafluoroethylene) (PTFE) with a ratio of 80:20 wt.% were prepared by rolling the paste and pressing the mixture onto a carbon paper. The mass loading of the carbon materials was approximately 0.5 mg cm⁻². Lithium foil of 1 cm² was used as an anode, and 60–70 μL of 1.0 M lithium nitrate (LiNO₃) in dimethylacetamide (DMA) was applied to each cell as an electrolyte. A glass fiber filter paper was used as a separator. The Li-O₂ batteries were assembled in 2032 coin cells with holes at the top in an Ar-filled glove box. The galvanostatic discharge-charge test was conducted using a Hokudo Denko Charge/Discharge system at room temperature in pure O₂ atmosphere.

2.5. Characterization

The specific surface area and pore size distribution of the microporous carbon were investigated by measuring the nitrogen adsorption and desorption isotherms at 77 K on a BELSORP-MAX (BEL, Japan). XRD analysis was carried out to characterize the pristine discharge products on a Bruker D8 Advanced diffractometer with Cu K α (λ = 1.5406 Å) radiation. The discharge products were examined by field emission scanning electron microscopy (SEM, JEOL 6700F). Field emission transmission electron microscopy (TEM, JEM 2100F, JEOL, Japan) was used to visualize the structure of the porous carbon.

3. Results and discussion

3.1. Morphology and structures of the prepared porous carbon materials

The morphology and structures of C-800, AC-950, and CMK-3 were observed using SEM and TEM. Fig. 1(a-c) contains SEM images of C-800, AC-950, and CMK-3, respectively. The C-800 and the AC-950 structures exhibit an elongated spherical shape with the particle size in the range of 1.0–2.5 μm. CMK-3 has a rod-like morphology with a uniform structure. The structure and size of the pores in C-800, AC-950, and CMK-3 were also examined by TEM. Fig. 1(d-f) shows high-resolution TEM images of all carbon materials. The image of the structure, C-800, reveals a typical microporous structure with a size of 0.5 nm. AC-950 shows a honeycomb-like pore structure with micro- and mesopores. These results indicate that the pores of C-800 and AC-950 produced from TCOPs having regular pore structures are well-ordered. In addition, CMK-3 has an ordered structure featuring linear arrays of mesopores of 6 nm divided by carbon walls, as shown in Fig. 1f.

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