



# Electrochemical Effects of Silicon/Diamond-Like Carbon Layered Composite on Oxygen Cathodes in Lithium–Oxygen Batteries



Sung Man Cho, Jun Kyu Lee, Woo Young Yoon\*

Department of Materials Science and Engineering, Korea University, 1, 5Ga, Anam-dong, Sungbuk-Gu, Seoul 136-701, Republic of Korea

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## ABSTRACT

Lithium–oxygen batteries are one of the most promising energy storage systems because of their high energy density. However, lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) and lithium carboxylates ( $\text{HCO}_2\text{Li}$ ,  $\text{CH}_3\text{CO}_2\text{Li}$ ) are formed on cycling, which results in high charging over-potential and limited cycle life. In this study, a silicon/diamond-like carbon (Si–DLC) coating film was deposited onto an  $\text{O}_2$  electrode uniformly by plasma-enhanced chemical vapor deposition to improve the electrochemical properties of lithium–oxygen batteries. The coated layer prevented the direct contact of carbon with both the  $\text{Li}_2\text{O}_2$  and the electrolyte, resulting in suppression of side-reaction product formation. For this reason, the coated cell showed better cycle life and round-trip efficiency than the pristine cell. When the charge was terminated, the potentials of the coated cell were 4.15 V for both the 1st and 5th cycles, whereas those of a pristine cell were 4.34 V for the 1st cycle and 4.51 V for the 5th cycle at a current density of  $100 \text{ mA g}^{-1}$  with a limited duration of 10 h for a single charge and discharge cycle. The coated cell was able to stably reach 50 cycles, whereas the pristine cell only lasted 7 cycles.

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## 1. Introduction

Lithium–oxygen batteries have attracted much attention owing to their high energy densities as compared to conventional lithium ion batteries, and they are one of the promising lithium secondary batteries for electric vehicles (EVs) and hybrid electric vehicles (HEVs) [1,2]. The theoretical specific energy and energy density of a Li– $\text{O}_2$  battery with the discharge reaction  $2\text{Li} + \text{O}_2 \rightarrow \text{Li}_2\text{O}_2$  are  $3505 \text{ Wh kg}^{-1}$  and  $3436 \text{ Wh l}^{-1}$ , respectively (including  $\text{O}_2$ ).

However, the high over-potential, low power density, and limited cycle life [3,4] of these batteries have prevented their commercialization. Many studies have attempted to address these problems, some of which used structure optimization of the porous  $\text{O}_2$  cathode [5–9], alternative catalytic materials [10–13], development of a stable electrolyte [14–16], and safety improvements to the lithium anode [17,18]. The problem in particular is that continuous carbon decomposition and electrolyte decomposition during cycling result in the formation of side products, which in turn give rise to the high over-potential. The carbon electrode reacts with  $\text{Li}_2\text{O}_2$  and promotes electrolyte decomposition during cycling in the Li– $\text{O}_2$  cell, which produces lithium carbonate ( $\text{Li}_2\text{CO}_3$ ), lithium formate monohydrate ( $\text{HCO}_2\text{Li}$ ), and lithium

acetate ( $\text{CH}_3\text{CO}_2\text{Li}$ ). The mechanism of carbon decomposition is:  $\text{Li}_2\text{O}_2 + \text{C} + 1/2\text{O}_2 \rightarrow \text{Li}_2\text{CO}_3$ . In the case of electrolyte decomposition, the mechanism of the side reaction is not identified clearly. These side products accumulate continuously during cycling and result in limited cycle life and increased charge potential of the Li– $\text{O}_2$  cell [19,20]. There have been several studies to suppress this side reaction. Bruce et al. used materials other than carbon black, such as TiC and nanoporous gold, as a conductive material. They reported Li– $\text{O}_2$  cells with TiC and nanoporous gold electrodes with respective capacity retentions of >98% and >95% after 100 cycles [21,22]. Lee et al. did not use a conductive material but instead deposited a cobalt oxide catalyst directly onto the cathode collector without using carbon black. The Li– $\text{O}_2$  cell with a carbon-free electrode showed a lower charge potential ( $\sim 3.83 \text{ V}$  vs.  $\text{Li}/\text{Li}^+$ ) than that with a carbon-only electrode ( $\sim 4.35 \text{ V}$  vs.  $\text{Li}/\text{Li}^+$ ) [23]. However, carbon is an attractive material; it has a large specific surface area owing to its porous structure, which is related to high energy density. Therefore, carbon is not a material that can be abandoned in Li– $\text{O}_2$  batteries.

In this work, we investigated a carbon cathode produced with a silicon/diamond-like carbon (Si–DLC) coating in order to suppress the side reactions in Li– $\text{O}_2$  cells. Si–DLC thin films are well known for chemical inertness and having good mechanical property such as high hardness [24–28]. Therefore, we expected that a Si–DLC thin film on a carbon cathode would have a positive effect on the cycling process. Si–DLC's property, particularly its chemical

\* Corresponding author. Tel.: +82 2 3290 3274; fax: +82 2 928 3584.  
E-mail address: [wyyoon@korea.ac.kr](mailto:wyyoon@korea.ac.kr) (W.Y. Yoon).

inertness should contribute to the enhancement of the electrochemical performance of the Li–O<sub>2</sub> cell.

The Li–O<sub>2</sub> cell with a Si–DLC-coated cathode showed better cycle life and lower charging polarization as compared to the uncoated cell. The electrochemical properties of the Li–O<sub>2</sub> cell with a Si–DLC-coated cathode were investigated and compared to those of an uncoated carbon cathode.

## 2. Experimental

### 2.1. Preparation of coated O<sub>2</sub> cathode

Polyvinylidene fluoride (PVDF) was dissolved in an N-methyl-2-pyrrolidone (NMP) solvent. Ketchenblack<sup>®</sup> (KB) carbon (EC600-JD, Ketjen Black Int. Co.; specific surface area 1270 m<sup>2</sup> g<sup>-1</sup>) and gamma manganese dioxide ( $\gamma$ -MnO<sub>2</sub>, Junsei Chemical Co., Ltd.) were mixed with a PVDF/NMP solution to fabricate a composite cathode in a jade bowl. KB carbon is used as a conducting agent. The  $\gamma$ -MnO<sub>2</sub> and PVDF are used as a catalyst and binder, respectively. The weight ratio of the cathode materials was 4:4:2 (KB: $\gamma$ -MnO<sub>2</sub>:PVDF). The mixed slurry was coated onto a nickel foam collector to a thickness of  $\sim$ 100  $\mu$ m by the doctor blade method (area of cathode:  $\sim$ 1.54 cm<sup>2</sup>). After loading the cathode materials, the electrode was blew by air gun to retain oxygen pathway, then was dried thoroughly in a vacuum at 80 °C for 24 h. The prepared electrodes had a carbon loading density of  $1.0 \pm 0.2$  mg cm<sup>-2</sup>. Finally, the Si–DLC thin film was deposited by plasma-enhanced chemical vapor deposition (PECVD) at 100 °C for 5 min (at Dongwoo Surface Tech Co., Ltd.). The source gases used were hydrocarbon (C<sub>2</sub>H<sub>2</sub>) and hexamethyldisiloxane (HMDSO). Fig. 1 shows the scheme of the PECVD setup.

### 2.2. Characterization of the O<sub>2</sub> cathode

The morphology of the O<sub>2</sub> cathode was observed using a scanning electron microscope (SEM, Hitachi S-4300, Japan) and a high-resolution transmission electron microscope (HR-TEM). Raman spectroscopy was performed to analyze the DLC, and time-of-flight secondary ion mass spectrometry (TOF-SIMS) analysis was carried out for mapping the distribution of constituents at the surface of the cathode, using a TOF-SIMS5 instrument (IONTOF, Germany). Fourier transform infrared (FTIR) spectroscopy was performed to analyze the surface of the

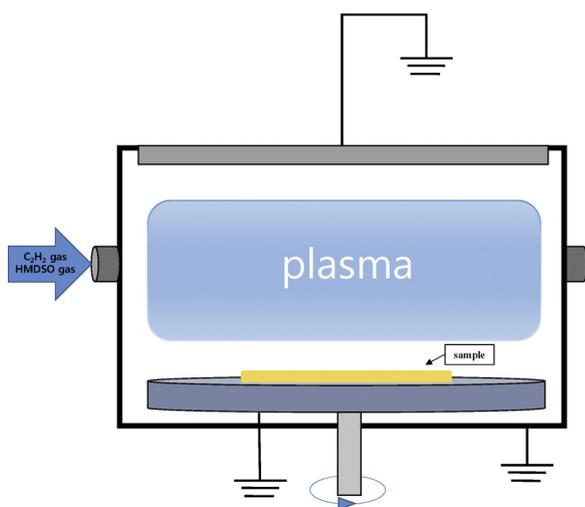


Fig. 1. Schematic diagram of PECVD equipment for Si–DLC coatings.

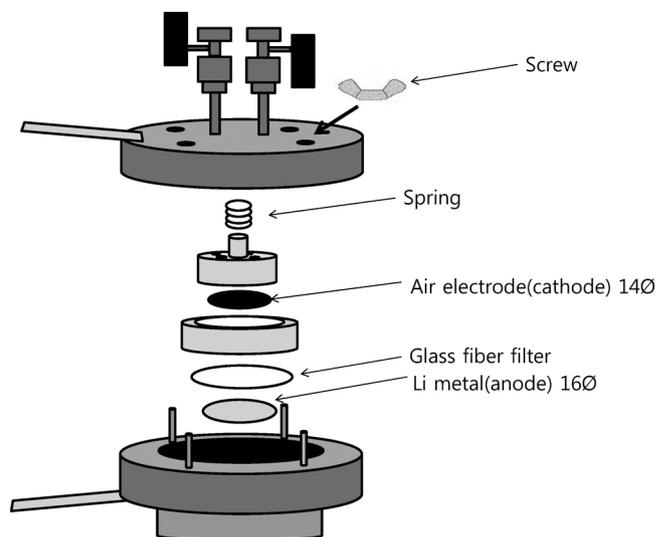


Fig. 2. Construction and design of the Li–O<sub>2</sub> cell.

cathode after cycling by using an FT-IR 4100 instrument (Jasco, Japan).

### 2.3. Cell assembly and electrochemical tests

Li–O<sub>2</sub> cells were assembled using an HS flat cell (Hohsen Co., Japan) under argon atmosphere in a glove box. The cell filled with electrolyte included an O<sub>2</sub> cathode, a Li metal anode, and glass microfiber filter paper (Whatman<sup>®</sup> GF/C) impregnated with the electrolyte. The electrolyte was composed of 1 M lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) salt in a tetraethylene glycol dimethyl ether (TEGDME) solvent. Construction and design of the cell are shown in Fig. 2. Electrochemical tests were performed at a current density of 100 mA g<sup>-1</sup><sub>carbon</sub> for a limited duration of 10 h for a single charge and discharge cycle. The

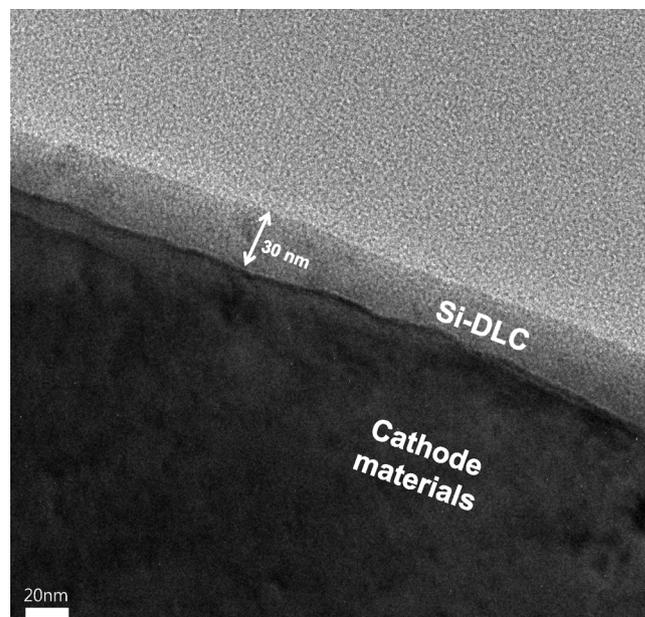


Fig. 3. TEM image of the Si–DLC-coated electrode.

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