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**MESOPOROUS NITROGEN DOPED CARBON-GLASS
CERAMIC CATHODE FOR HIGH PERFORMANCE
LITHIUM-OXYGEN BATTERY (POSTPRINT)**

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Power and Control Division**

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14. ABSTRACT
The composite cathode prepared from highly mesoporous nitrogen doped carbon (N-C) blend and lithium aluminum germanium phosphate (LAGP)-glass ceramic has been explored for its application in an all solid-state lithium-oxygen cell. The composite cathode exhibits remarkable enhancement in cell capacity in comparison to N-C blend cathode. This enhancement is ascribed to the mesoporous structure and higher electrocatalytic activity of cathode materials as well as fast lithium ion conduction of LAGP in the cathode.

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Mesoporous Nitrogen Doped Carbon-Glass Ceramic Cathode for High Performance Lithium-Oxygen Battery

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Abstract: *The composite cathode prepared from highly mesoporous nitrogen doped carbon (N-C) blend and lithium aluminum germanium phosphate (LAGP)-glass ceramic has been explored for its application in an all solid-state lithium-oxygen cell. The composite cathode exhibits remarkable enhancement in cell capacity in comparison to N-C blend cathode. This enhancement is ascribed to the mesoporous structure and higher electro-catalytic activity of cathode materials as well as fast lithium ion conduction of LAGP in the cathode.*

Keywords: Nitrogen doped carbon; glass-ceramic; scanning electron microscopy; oxygen reduction; lithium-oxygen battery.

Introduction

In recent years, lithium-oxygen batteries [1] have been the focus of intense scientific interest due to its high specific energy [2]. Development of these batteries is very attractive as it uses environmental friendly and abundant atmospheric oxygen. Cathode reaction proceeds with the reduction of readily available oxygen from the atmosphere. This active material is not stored inside battery, thereby increasing its specific energy. Although these batteries offer many advantages, they also face many technical challenges that need to be overcome for realization of practical lithium-oxygen battery operating in an ambient environment. Several factors dictate the performance of these batteries such as air cathode and electrolyte composition, relative humidity, cell designs, etc. In particular, the material architecture of air cathode plays a critical role for reduction and diffusion of oxygen in the cathode of lithium-oxygen battery.

In 1996, Abraham and Jiang [3] first reported a nonaqueous, rechargeable lithium-oxygen cell that delivered cell capacities of 1410 mAh/g in pure oxygen atmosphere. Following this work, there have been significant efforts to improve cell capacity [4,5]. These studies have been focused on cathode formulation [6,7,8,9,10], efficient oxygen reduction catalysts [11,12], electrolyte compositions [13,14], effect of moisture [15], etc. Recently, lithium-oxygen batteries were reported using air cathodes made from carbon nanotubes [16,17], graphene [18,19] and a mixture of carbon nanotubes and carbon fibers [20].

In our previous studies on a fully solid-state, rechargeable lithium-oxygen cells [21,22], we have found that these cells fabricated from carbon and lithium aluminum germanium phosphate (LAGP) demonstrated an excellent discharge capacity. In subsequent work [23,24], we further reported enhancement in discharge capacity prepared from nitrogen doped carbon (N-C) blend with 5 wt % LAGP (composite **1**) and N-C blend with 10 wt % LAGP (composite **2**). The improvement in cell capacity is due to the superior electrochemical activity of nitrogen doped carbon materials [23,25,26] and the superior ionic conductivity of LAGP to transport lithium ions as well as the reduction of oxygen [27]. In continuation, we examined the use of N-C blend with 20 wt % LAGP (composite **3**) in the cathode of a solid-state lithium-oxygen cell and compared the cell performance with composite **1** and composite **2**. Furthermore, the role of porosity, surface area and electro-catalytic activity on the electrochemical performance is also discussed.

Experimental details

Commercially available Ketjenblack (KB) EC 600 JD and Calgon activated (CA) carbon were used to prepare N-C blend as reported previously [23]. Lisicon glass-ceramic, LAGP, was fabricated as described in our earlier work [28].

A scanning electron microscope (SEM, JEOL JSM-6060) equipped with energy dispersive X-ray (EDX) spectroscopy assembly was used to observe the morphologies of the specimens. Structure and purity of these materials were performed by powder X-ray diffraction (XRD) on a Rigaku D/MAX-2250 diffractometer fitted with CuK α as a radiation source at 40 kV and 40 mA. The surface areas of the specimens were determined by nitrogen adsorption / desorption measurements at 77 K (Micromeritics ASAP 2020). The porosity of cathode material was characterized by a gas pycnometer (Micromeritics, Accu Pyc II 1340). Thermogravimetric analysis (TGA) was performed on approximately 10 mg of the specimen on a thermogravimetric analyzer (TA Instruments, model 2050). Cyclic voltammetry (CV) and galvanostatic charge-discharge measurements of the specimen were conducted using a computer controlled VersaSTAT 4 (Princeton Applied Research) electrochemical workstation. CV measurements were performed in a

standard three-electrode cell configuration using 0.1 M KOH as the electrolyte at 25 °C with a scan rate of 5 mV/sec. The working electrode for CV measurement was prepared by spreading the paste of composite **3** and Nafion (tetrafluoroethylene based fluoropolymer-copolymer) on the tip of a graphite rod. A Pt wire was used as the counter electrode. All potentials were measured with respect to saturated calomel electrode (SCE).

Composite **3** air cathodes were fabricated from a mixture of N-C blend and 20 wt % LAGP. N-C blend was prepared from N-KB and N-CA carbon in a 40:60 wt % ratio. N-C and LAGP powders with a polytetrafluoroethylene (PTFE) suspension were ball milled and mixed with de-ionized water to obtain a soft mass. This solid paste was then spread on a nickel foam and pressed by sandwiching between two stainless steel plates at 1 MPa. The cathode specimen was dried overnight at 100 °C under vacuum. A solid-state lithium-oxygen cell with a 2 cm² area was fabricated using a commercially available cell casing in a dry room with controlled moisture content. Composite **3** films on nickel foam were used as working cathodes along with lithium metal as anode and the polymer-coated LAGP as electrolyte. The processing and properties of the polymer-coated LAGP have been reported and described in our earlier work [21].

Electrochemical impedance spectroscopy (EIS) measurements on the lithium-oxygen cells were conducted over a frequency range of 0.1 Hz to 10⁶ Hz before and after discharge measurements. All electrochemical tests on these cells were carried under oxygen atmosphere.

Results and discussion

The morphology of the working cathode was examined under SEM. Figure 1 shows the SEM micrograph of composite **3** that contains both fibrous structure of N-C carbon and crystals of LAGP (shown by arrow).

TGA (not shown here) conducted on composite **3** in air shows that the sample mass does not change with temperature below 500°C. Significant mass loss occurs at about 550°C. This is due to the carbonization reaction involving breakage of C-C bonds and C-N bonds. TGA shows that above 650°C there is no further weight loss.

A typical nitrogen adsorption – desorption isotherm at 77 K for composite **3** is shown in Figure 2. Isotherm shows adsorption hysteresis indicating the presence of mesopores. The Brunauer-Emmett-Teller (BET) surface area, pore volume, and porosity of composite **3** were found to be 970 m²/g, 1.25 cm³/g, and 40.8 %, respectively.

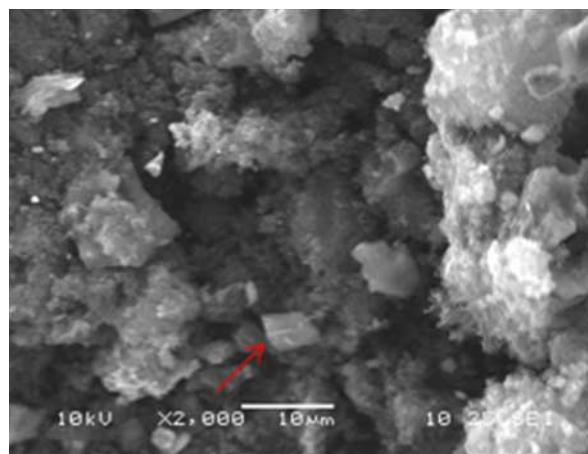


Figure 1. SEM image of composite **3** (N-C blend and 20 wt % of LAGP).

The remarkable nitrogen uptake above the relative pressure ratio of 0.40 has been observed in BET isotherm and is due to the condensation of nitrogen in a mesoporous carbon.

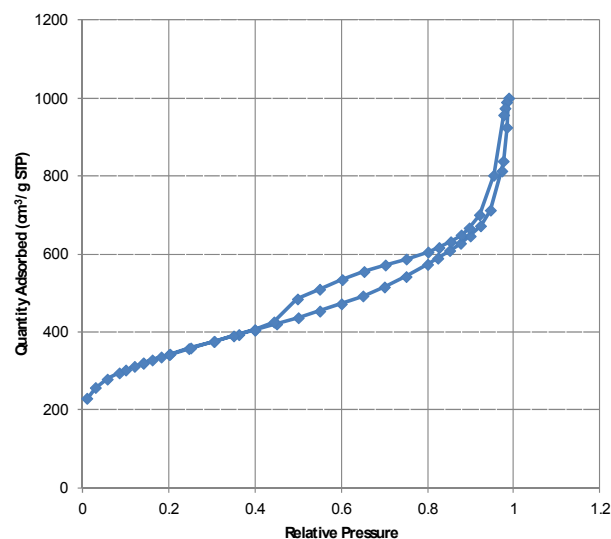


Figure 2. N₂ adsorption - desorption isotherm for composite **3** (N-C blend and 20 wt % of LAGP).

The CV curve recorded for composite **3** in oxygen saturated aqueous solution of 0.1 M KOH is presented in Figure 3. It also exhibits the CV curves for composite **1** and composite **2**. Well defined oxygen reduction reaction (ORR) peaks were observed at around -0.495 V, -0.468 V, -0.451 V (vs. SCE) for composites **1**, **2**, and **3**, respectively, with highest reduction current density of 0.0058 A/cm² for composite **3**. This indicates that composite **3** has a good electro-catalytic activity for ORR. No electro-catalytic activity was observed for all these cathode materials when the electrolyte was saturated with nitrogen.

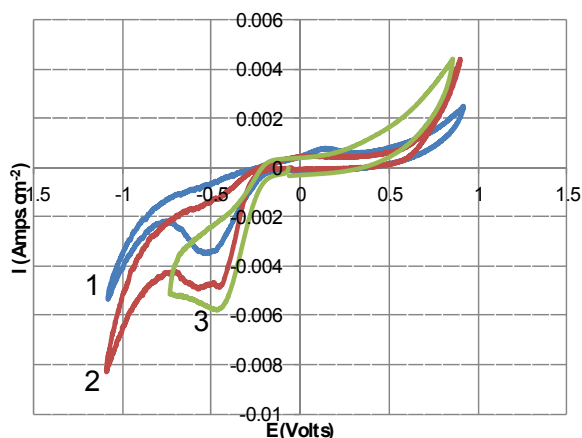


Figure 3. CV of (1) composite 1, (2) composite 2, and (3) composite 3 in oxygen saturated 0.1 M KOH at a scan rate of 5 mV/Sec at 25 °C.

Based on the high surface area, mesoporous structure as well as electro-catalytic activity towards oxygen reduction of composite 3, a solid-state lithium-oxygen cell with a 2 cm² area was fabricated (Figure 4).

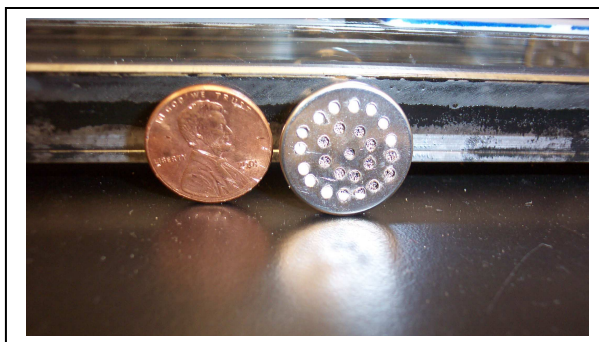


Figure 4. Photograph of a Solid-State lithium-oxygen cell.

The cathode side of the cell has perforations to access oxygen in the cathode. The lithium anode was coupled to an oxygen cathode through a solid electrolyte laminate as described in our previous work [21]. The solid electrolyte laminate provides very high ionic conductivity for transport of lithium ions from lithium anode to oxygen cathode. In addition, the electrolyte laminate improves lithium-electrolyte interfacial stability and passivates the lithium surface.

The electrochemical performance of composite 3 was evaluated as cathode in lithium-oxygen cell in oxygen atmosphere. Figure 5 shows the discharge profiles of the lithium-oxygen cells with composites 1, 2, and 3 cathodes. The cells were discharged using current of 0.2 mA at 75 °C. Cell with composite 3 as cathode delivers 10.5 mAh discharge cell capacity. On the other hand, under identical conditions cells composed of composites 1 and 2 as cathodes delivered 1.97 mAh, and 9.03 mAh discharge capacities, respectively [23,24]. The discharge

capacity of 1.44 mAh for the cell with cathode composed of N-C blend has been reported previously [23]. Thus, cell with composite 3 as cathode has seven times higher cell capacity than that of the cathode composed with N-C blend. Thus, an incremental increase of LAGP concentration in the cathode formulation enhances the discharge cell capacity. This enhancement in cell capacity is due to improved electro-catalytic activity and high mesoporosity of composite 3 as well as the fast lithium ion conduction deep inside the cathode. All these characteristics of composite 3 are indicative of high electro-catalytic sites to catalyze the discharge reactions. In addition, a higher porosity of cathode increases oxygen diffusivity in the cathode and accumulates the reaction products that help to improve the cell capacity. It is reported that the pores of different sizes are filled with discharge products at different rates [29] until air electrode cease functioning.

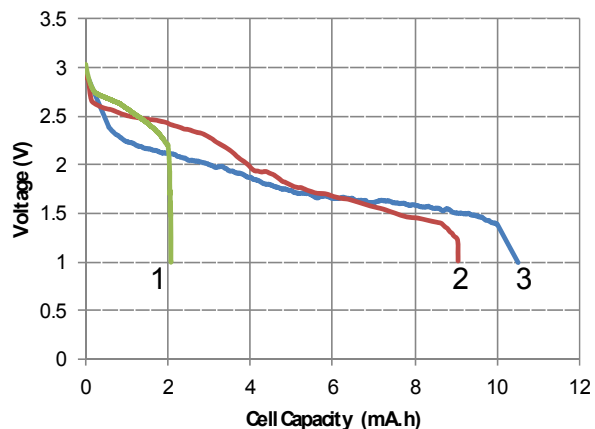


Figure 5. Discharge profiles for a lithium-oxygen cell at 75 °C using (1) composite 1, (2) composite 2, and (3) composite 3 as cathode in oxygen atmosphere.

Figure 5 also shows that there is significant potential drop during an initial stage of discharge due to activation barrier of cathode chemistry that includes the series resistances between various cell components. Further research work to engineer cathode architecture and improve the cell performance of lithium-oxygen batteries is currently underway.

Conclusion

In conclusion, this work demonstrates significant improvement in cell performance of lithium-oxygen cell with cathode formulation of composite 3. The discharge cell capacity of this cell is 10.5 mAh and indicates the potential of composite 3 as a promising cathode material for lithium-oxygen cells.

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