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**MESOPOROUS NITROGEN-DOPED CARBON-GLASS
CERAMIC CATHODES FOR SOLID-STATE
LITHIUM-OXYGEN BATTERIES (Postprint)**

Padmakar Kichambare and Stanley Rodrigues

**Thermal & Electrochemical Branch
Energy/Power/Thermal Division**

Jitendra Kumar

University of Dayton Research Institute

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Mesoporous Nitrogen-Doped Carbon-Glass Ceramic Cathodes for Solid-State Lithium–Oxygen Batteries

Padmakar Kichambare,^{*,†} Stanley Rodrigues,[†] and Jitendra Kumar[‡]

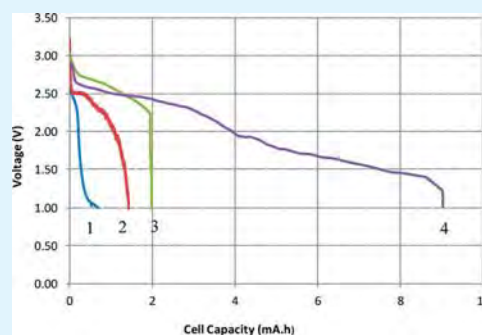
[†]Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base, Ohio 45433-7252, United States

[‡]Electrochemical Power Group, University of Dayton Research Institute, 300 College Park, Dayton, Ohio 45469-0170, United States

Supporting Information

ABSTRACT: The composite of nitrogen-doped carbon (N–C) blend with lithium aluminum germanium phosphate (LAGP) was studied as cathode material in a solid-state lithium–oxygen cell. Composite electrodes exhibit high electrochemical activity toward oxygen reduction. Compared to the cell capacity of N–C blend cathode, N–C/LAGP composite cathode exhibits six times higher discharge cell capacity. A significant enhancement in cell capacity is attributed to higher electrocatalytic activity and fast lithium ion conduction ability of LAGP in the cathode.

KEYWORDS: nitrogen-doped mesoporous carbon, lithium–air, electrochemical impedance spectroscopy, discharge cell capacity, solid-state lithium–oxygen battery



There is a great deal of interest in lithium–oxygen batteries as one of the most promising high-energy-density electrochemical power sources anticipated to impact future battery technologies.^{1,2} Because of their high specific capacity, the lithium–oxygen batteries could reach an energy density higher than conventional electrochemical energy storage devices.³ Although these batteries have unprecedented theoretical energy densities of 11 000 Wh/kg,⁴ there are significant technical challenges confronting the development of practical lithium–oxygen batteries operating in an ambient environment.^{5,6} Some of the major challenges are the strong polarization at the cathode due to deposition of discharge products in the oxygen electrodes and anode passivation due to moisture contamination. Motivated by the pioneering work of Abraham and Jiang,⁴ wherein they reported the first non-aqueous, rechargeable lithium–oxygen cell, considerable research efforts are being directed toward the development of lithium–oxygen cell.^{7–14} The cathode formulation and electrolyte composition on discharge capacity and rechargeability have been the main focus in these investigations. The diffusion and reduction of oxygen in the cathode play a key role in operational lifetime of these cells. Oxygen reduction reaction (ORR) on the cathode is sluggish in nature and a rate-determining step that limits the performance of the cathode in optimizing the power output.

Recently, it was demonstrated that the nitrogen doping of carbon materials have the superior electrochemical activity of carbon for oxygen reduction^{15,16} and this feature of doping nitrogen into carbon materials is found to be useful for

enhancement of discharge cell capacity.^{10,11} It has been reported that the lithium aluminum germanium phosphate (LAGP)-glass ceramics has the ability not only to transport lithium ions but also to facilitate reduction of oxygen in lithium–oxygen cell.¹⁷ In addition, the nitrogen doped carbon (N–C) blend is mesoporous and has an excellent chemical and thermal stability for electrocatalysis.¹⁸ Important figure of merit for the design of lithium–oxygen cell is the access of oxygen to the reaction sites to facilitate the reduction of oxygen in the cathode. N–C blend with high porosity will promote the access of oxygen to the reaction sites inside the pores of carbon, while ORR activity of N–C blend and LAGP should serve as effective electrocatalyst for reduction of oxygen. Here, we extend our study to report the use of a composite prepared from N–C blend and LAGP in the cathode of a solid-state lithium–oxygen cell. Incorporation of LAGP additive by physical admixture into the N–C blend leads to enhancement of the electrochemical performance of the lithium–oxygen cell. In this work, we have confined our results to only 5 and 10 wt % LAGP addition into N–C blend.

The working cathodes, namely, N–C blend with 5 wt % LAGP (composite 1) and N–C blend with 10 wt % LAGP (composite 2), were prepared. N–C blend was prepared from the mixture of nitrogen-doped Ketjenblack (N-KB) and nitrogen-doped Calgon-activated (N-CA) carbon in a 40:60

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wt % ratio. The weight of N–C blend on Ni foam was about 7 mg. The procedure for the preparation of N–C blend and LAGP has been described previously.^{10,17} The Brunauer–Emmett–Teller (BET) nitrogen adsorption–desorption isotherms of composite 1 (see Figure S1 in the Supporting Information) and composite 2 used as cathodes were obtained. Shown in Figure S2 (Supporting Information) is a typical mesopore size distribution of composite 1. BET surface areas for composite 1 and composite 2 are 999.8 and 974.35 m²g^{−1}, respectively, smaller than that of N–C blend (see Table S1 in the Supporting Information). On the other hand, the porosity values for N–C blend, composite 1, and composite 2 were found to be 42, 41.5, and 41%, respectively. The surface area and porosity in composite 1 and composite 2 help to improve the cell capacity of lithium–oxygen cell.

The electrocatalytic ability of composite 1 and composite 2 specimens were further evaluated. Shown in Figure 1 are the

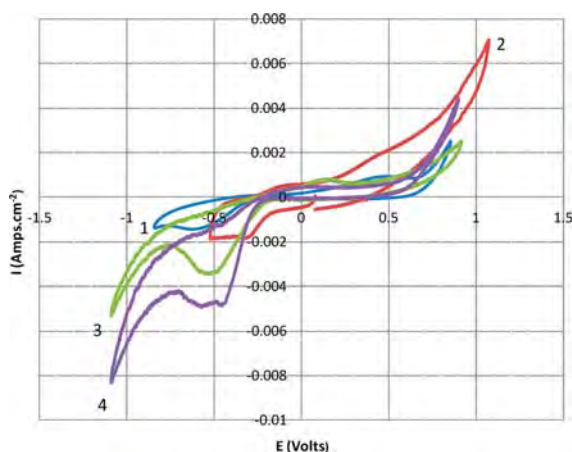


Figure 1. CV of (1) LAGP, (2) N–C blend, (3) composite 1, and (4) composite 2 in 0.1 M KOH at 25 °C at scan rate of 5 mV min^{−1}.

cyclic voltammograms (CVs) of these different electrodes with reference to the saturated calomel electrode (SCE) electrode in an oxygen saturated aqueous solution of 0.1 M KOH. No electrocatalytic activity is noted when the electrolyte was saturated with nitrogen. The ORR potential is about −0.45 V for N–C blend electrode, −0.495 V for composite 1 electrode, −0.568 V for composite 2 electrode and −0.6 V for LAGP. The ORR potentials of composite 1 and composite 2 are lower than that of N–C blend electrode, while current density for composite 1 electrode and composite 2 electrode were found to be two and three times larger than that of N–C blend electrode, respectively, indicating that the addition of LAGP into N–C blend enhances the electrocatalytic activity. These results are in good agreement with the results reported in literature.^{15,16} It is also observed from Figure 1 that the LAGP electrode exhibits not only a cathodic peak (−0.6 V) but also an anodic peak at 0.5 V. The cathodic and anodic peak intensities are 1.4 and 0.9 mA cm^{−2}, respectively. There is an asymmetry in the peak locations and intensities that points out a possibility of irreversibility of the reactions.

On the basis of highly mesoporous structure and the superior electrocatalytic performance of composite 1 and composite 2 in ORR, a solid-state lithium–oxygen cell with a 2 cm² area was fabricated in a commercially available cell casing under dry

argon atmosphere. Figure 2a displays a typical low magnification scanning electron microscopy (SEM) image of nickel foam

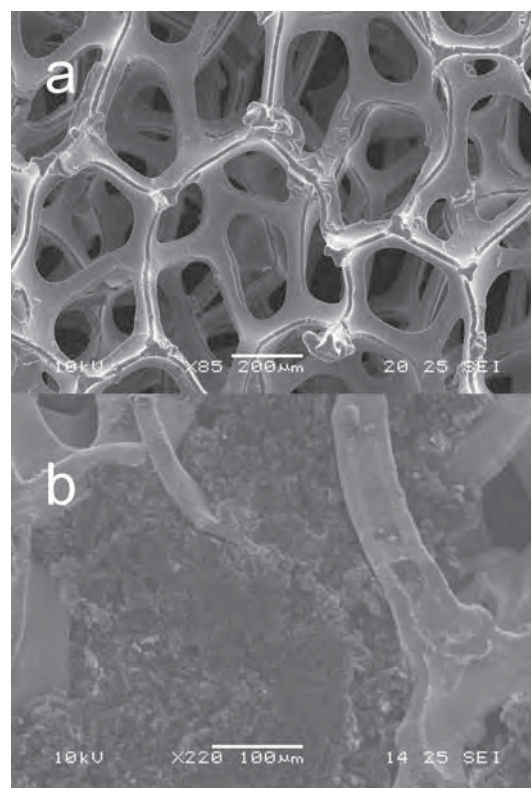


Figure 2. SEM images of (a) nickel foam and (b) oxygen cathode with composite 2.

used in the fabrication and reveals the presence of highly open framework of nickel for a fast diffusion of oxygen. Shown in Figure 2b is a typical SEM image of composite 2 inside the nickel foam. A solid electrolyte LAGP reported in previous work¹⁹ was used to couple the lithium anode with an oxygen cathode and was found to be stable if discharged to 1 V. The electrochemical performance of the composite 1 and composite 2 as cathodes in lithium–oxygen battery was evaluated under oxygen atmosphere. Figure 3 shows the discharge capacities of the lithium–oxygen cells with cathode composed of the composite 1 and composite 2 at the discharge current of 0.2 mA at 75 °C. Figure 3 also depicts the discharge cell capacities of the lithium–oxygen cells with cathodes composed of N–C blend and blend of KB and CA carbon (C blend) reported in our earlier work.¹⁰ Cells composed of composite 1 and composite 2 delivers 1.97 mAh and 9.03 mAh discharge cell capacities, respectively. On the other hand, the N–C and C blend cathode under identical conditions delivered 1.44 mAh and 0.70 mAh cell capacity, respectively.¹⁰ Cells composed of composite 1 and composite 2 has 1.3 and 6 times higher cell capacity than that of the cathode composed of N–C blend, respectively. This enhancement in cell capacity is ascribed to improved electrocatalytic activity of composite 1 and composite 2 that help facilitate the cathodic reactions. Incorporation of 10 wt % of LAGP in N–C blend improves the fast lithium ions conduction deep inside the oxygen cathode and further

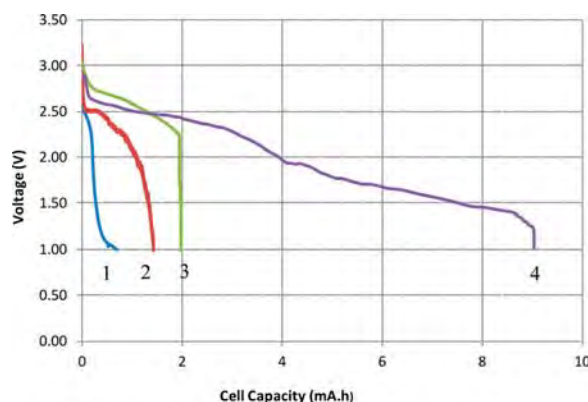


Figure 3. Discharge curves of lithium–oxygen cell with discharge current of 0.2 mA at 75 °C for (1) C blend, (2) N–C blend, (3) composite 1, and (4) composite 2.

enhances the cell capacity as shown in Figure 3. Thus, an increase of LAGP concentration in the cathode formulation increases the discharge cell capacity. Our results are consistent with previous work²⁰ wherein, an incremental increase up to 77 wt % of LAGP in cathode formulation (C blend) is reported. However, an increase in LAGP loading increases the total weight of cathode and lowers gravimetric energy density of the cells. In the present work, the efforts are directed to achieve similar discharge cell capacity with lower wt % of LAGP in cathode formulation.

LAGP shows electrocatalytic activity toward oxygen reduction.¹⁷ In addition, LAGP serves a dual role in these cells. First, as an electrolyte, LAGP transports Li^+ ions from lithium anode to cathode (ionic conductivity²¹ $\sigma = 4.22 \times 10^{-3}$ S/cm at 27 °C). Second, in the cathode, it facilitates a fast conduction of Li^+ ions deep inside the cathode matrix. The existence of cavities and tunnels in structure of LAGP accommodates gaseous oxygen molecules and helps improve the diffusion as well as reduction of oxygen in the cathodes. Thus, the composite 2 affords high electrocatalytic sites to catalyze the discharge reaction, leading to the favorable oxygen reduction activity and higher discharge cell capacity.

Apart from higher electrochemical activity of the composite 1 and composite 2, the electrochemical performance of the lithium–oxygen cell also depends on the porosity of the oxygen electrode. Increase in the porosity of N–C blend with doping of nitrogen increases higher oxygen diffusivity in the composite 1 and composite 2 that enhances the cell capacity. A gradual decrease in cell discharge from 2.55 to 1.35 V is also observed in Figure 3 for the composite 2; while composite 1 shows a sharp cell discharge around 2.25 V. The N–C and C blend exhibits a low cell capacity with sharp discharges. Such type of flat plateau has been reported for lithium–oxygen cell when cell is discharged in oxygen atmosphere that involve formation of Li_2O_2 and/or Li_2O .^{22–24} Most recently, based on density functional theory and classical statistical analyses, it is reported that in Li_2O_2 , Li_2O , and LiO_2 are the most probable byproducts in lithium–oxygen cells.²⁵

Electrochemical impedance spectroscopy (EIS) is an effective technique for studying the properties at the electrode–electrolyte interface and the bulk electrolyte. EIS was used to analyze the impedance behavior of cathode in the lithium–oxygen cell before and after discharge. Nyquist plots before

discharge (see Figure S3 in the Supporting Information) exhibit a low charge-transfer resistance for the N–C blend, composite 1 and composite 2. This implies faster charge-transfer kinetics. Here the focus is to observe the change in the apparent diameter of the semicircle of the lithium–oxygen cell using EIS. The charge-transfer resistances of the lithium–oxygen cell fabricated with N–C blend, composites 1, and composite 2 are found to be smaller than that for the C blend. From the Nyquist plots obtained after discharge (Figure 4), the values of

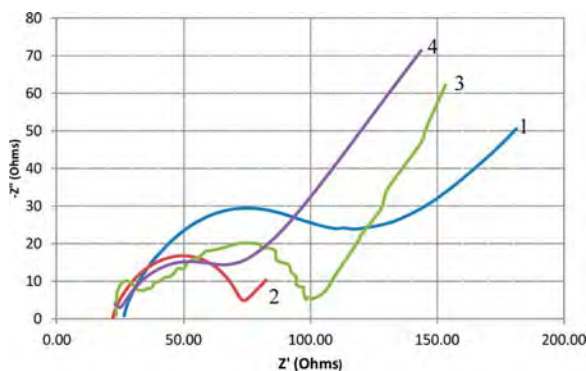


Figure 4. Nyquist plots of lithium–oxygen cell after discharge of cell at 75 °C for (1) C blend, (2) N–C blend, (3) composite 1, and (4) composite 2.

diameter were determined to be 93 and 58 Ω for the cell with composite 1 and composite 2, respectively. The value of diameter for the C blend and N–C blend were 130 and 55 Ω , respectively. This increase in resistance of the oxygen cathode is due to the formation of discharge products in the pores of the cathode. EIS results combined with CV experiments lead to the conclusion that the N–C blend, composite 1, and composite 2 demonstrates higher catalytic activity toward the ORR in the oxygen cathode, thereby improving the cell capacity of lithium–oxygen cell.

In summary, this work demonstrates remarkable improvement in cell performance of lithium–oxygen cell using the combination of N–C blend with LAGP. The discharge cell capacity strongly depends on the surface area, porosity and electrocatalytic activity of composite 1 and composite 2. A comparison of both composites studied in this work indicates that composite 2 is a promising cathode material for lithium–oxygen batteries.

■ ASSOCIATED CONTENT

● Supporting Information

Experimental details, fabrication of air cathode, and physical and electrochemical characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Padmakar.Kichambare@WPAFB.AF.MIL.

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