



**AFRL-RQ-WP-TP-2015-0054**

**MESOPOROUS NITROGEN-DOPED CARBON-LiSICON  
GLASS CERAMICS AS HIGH PERFORMANCE  
CATHODES IN SOLID-STATE LITHIUM-OXYGEN  
BATTERIES (POSTPRINT)**

**Padmakar Kichambare and Stanley Rodrigues**

**Electrical Systems Branch  
Power and Control Division**

**MARCH 2013**

**Approved for public release; distribution unlimited.**

*See additional restrictions described on inside pages*

**STINFO COPY**

**© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim**

**AIR FORCE RESEARCH LABORATORY  
AEROSPACE SYSTEMS DIRECTORATE  
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7541  
AIR FORCE MATERIEL COMMAND  
UNITED STATES AIR FORCE**

## NOTICE AND SIGNATURE PAGE

Using Government drawings, specifications, or other data included in this document for any purpose other than Government procurement does not in any way obligate the U.S. Government. The fact that the Government formulated or supplied the drawings, specifications, or other data does not license the holder or any other person or corporation; or convey any rights or permission to manufacture, use, or sell any patented invention that may relate to them.

This report was cleared for public release by the USAF 88th Air Base Wing (88 ABW) Public Affairs Office (PAO) and is available to the general public, including foreign nationals.

Copies may be obtained from the Defense Technical Information Center (DTIC)  
(<http://www.dtic.mil>).

AFRL-RQ-WP-TP-2015-0054 HAS BEEN REVIEWED AND IS APPROVED FOR PUBLICATION IN ACCORDANCE WITH ASSIGNED DISTRIBUTION STATEMENT.

*//Signature//*

---

STANLEY J. RODRIGUES  
Project Manager  
Electrical Systems Branch  
Power and Control Division

*//Signature//*

---

GREGORY L. FRONISTA, Chief  
Electrical Systems Branch  
Power and Control Division  
Aerospace Systems Directorate

*//Signature//*

---

DANIEL B. THOMPSON  
Acting Division Chief  
Power and Control Division  
Aerospace Systems Directorate

This report is published in the interest of scientific and technical information exchange, and its publication does not constitute the Government's approval or disapproval of its ideas or findings.

\*Disseminated copies will show "*//Signature//*" stamped or typed above the signature blocks.

# REPORT DOCUMENTATION PAGE

*Form Approved*  
OMB No. 0704-0188

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

<b>1. REPORT DATE (DD-MM-YY)</b> March 2013		<b>2. REPORT TYPE</b> Journal Article Postprint		<b>3. DATES COVERED (From - To)</b> 01 March 2013 – 01 March 2013	
<b>4. TITLE AND SUBTITLE</b> MESOPOROUS NITROGEN-DOPED CARBON-LiSICON GLASS CERAMICS AS HIGH PERFORMANCE CATHODES IN SOLID-STATE LITHIUM-OXYGEN BATTERIES (POSTPRINT)				<b>5a. CONTRACT NUMBER</b> In-house	
				<b>5b. GRANT NUMBER</b>	
				<b>5c. PROGRAM ELEMENT NUMBER</b> 62203F	
<b>6. AUTHOR(S)</b> Padmakar Kichambare and Stanley Rodrigues (AFRL/RQQE)				<b>5d. PROJECT NUMBER</b> 3145	
				<b>5e. TASK NUMBER</b> N/A	
				<b>5f. WORK UNIT NUMBER</b> Q10H	
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> Electrical Systems Branch (AFRL/RQQE) Power and Control Division, Air Force Research Laboratory Aerospace Systems Directorate Wright-Patterson Air Force Base, OH 45433-7541 Air Force Materiel Command, United States Air Force				<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b>  AFRL-RQ-WP-TP-2015-0054	
<b>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b> Air Force Research Laboratory Aerospace Systems Directorate Wright-Patterson Air Force Base, OH 45433-7541 Air Force Materiel Command United States Air Force				<b>10. SPONSORING/MONITORING AGENCY ACRONYM(S)</b> AFRL/RQQE	
				<b>11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S)</b> AFRL-RQ-WP-TP-2015-0054	
<b>12. DISTRIBUTION/AVAILABILITY STATEMENT</b> Approved for public release; distribution unlimited.					
<b>13. SUPPLEMENTARY NOTES</b> PA Case Number: 88ABW-2013-0771; Clearance Date: 15 Feb 2013.  Report published in <i>Energy Technology</i> Vol. 1, 2013. © 2013 Wiley-VCH Verlag GmbH&Co. KGaA, Weinheim. The U.S. Government is joint author of the work and has the right to use, modify, reproduce, release, perform, display, or disclose the work.					
<b>14. ABSTRACT</b> Here we report the use of N-C blend with 20 wt% LAGP (composite 3) in the cathode of a solid-state lithium-oxygen cell with superior discharge cell capacity compared to the cell performance with composite 1 and composite 2. The improvement in cell performance is due to the superior electrochemical activity of composite 3 for the reduction of oxygen and the higher ionic conductivity of LAGP to transport lithium ions in the composite matrix.					
<b>15. SUBJECT TERMS</b> lithium-oxygen battery, oxygen reduction reactions, nitrogen-doped carbon, lithium aluminum germanium phosphate					
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT:</b> SAR	<b>18. NUMBER OF PAGES</b> 10	<b>19a. NAME OF RESPONSIBLE PERSON (Monitor)</b> Stanley J. Rodrigues <b>19b. TELEPHONE NUMBER (Include Area Code)</b> N/A
<b>a. REPORT</b> Unclassified	<b>b. ABSTRACT</b> Unclassified	<b>c. THIS PAGE</b> Unclassified			

DOI: 10.1002/ente.201200028

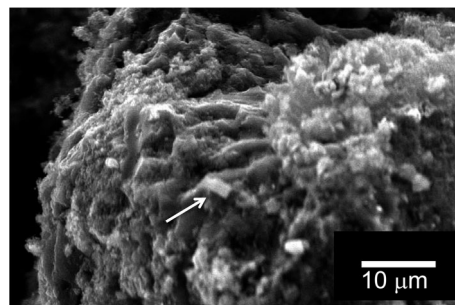
# Mesoporous Nitrogen-Doped Carbon-LiSiCON Glass Ceramics as High Performance Cathodes in Solid-State Lithium–Oxygen Batteries

Padmakar Kichambare\* and Stanley Rodrigues<sup>[a]</sup>

The vast increase in demand for energy has generated a large need for energy storage devices that have high energy and power densities. Among various electrochemical energy storage systems explored to date, the lithium–oxygen battery is one of the most promising technologies,<sup>[1]</sup> which is attracting a great deal of attention because of its high theoretical specific capacity.<sup>[2]</sup> Although these batteries offer many advantages, they also face many technical challenges that need to be overcome for the realization of practical lithium–oxygen cells operating in ambient environments. Several components dictate the performance of these cells, such as the oxygen cathode, electrolyte composition, relative humidity, and cell design.<sup>[3]</sup> In particular, the material architecture of the oxygen cathode plays a critical role for the reduction and diffusion of oxygen in the cathode of a lithium–oxygen cell.

In 1996, Abraham and Jiang<sup>[4]</sup> first reported a nonaqueous, rechargeable lithium–oxygen cell that delivered a cell capacity of 1410 mAhg<sup>-1</sup> in a pure oxygen atmosphere. Following this work, there have been significant efforts to improve the cell capacity.<sup>[5]</sup> In our previous studies regarding solid-state, rechargeable lithium–oxygen cells,<sup>[6]</sup> we found that cells fabricated from carbon and lithium aluminum germanium phosphate (LAGP) demonstrated excellent discharge capacities. In subsequent work,<sup>[7,8]</sup> we reported an enhancement in discharge capacity for a cell prepared from a nitrogen-doped carbon (N–C) blend with 5 wt % LAGP (composite **1**), and a N–C blend with 10 wt % LAGP (composite **2**). In continuation, we report here the use of a N–C blend with 20 wt % LAGP (composite **3**) in the cathode of a solid-state lithium–oxygen cell that demonstrates superior discharge cell capacity compared to the cell performance with composite **1** or **2**. The improvement in cell performance is attributed to superior electrochemical activity of composite **3** towards the reduction of oxygen, and the higher ionic conductivity of LAGP to transport lithium ions throughout the composite matrix.

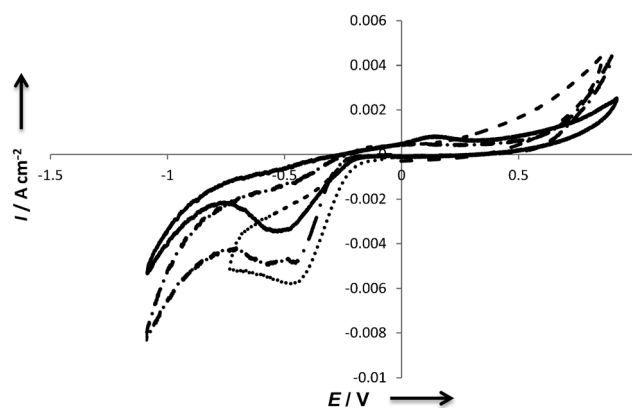
The morphology of composite **3** was examined by using SEM. Figure 1 shows the SEM image of composite **3**, the image contains fibrous structures that correspond to the N–C blend, and crystals of LAGP (shown by the arrow). Typical Brunauer–Emmett–Teller (BET) nitrogen adsorption–desorption data and the mesopore size distribution at 77 K for composite **3** are shown in Figures S1 and S2, respectively (see the Supporting Information). The BET surface



**Figure 1.** SEM image of composite **3** (N–C blend and 20 wt % LAGP), which shows both fibrous and crystalline (see the arrow) material.

area, pore volume, and porosity of composite **3** were demonstrated to be 970 m<sup>2</sup>g<sup>-1</sup>, 1.25 cm<sup>3</sup>g<sup>-1</sup>, and 40.8%, respectively.

Cyclic voltammetry (CV) was used to evaluate the electrocatalytic activity of composite **3**. The CV curves recorded in an oxygen-saturated aqueous solution of 0.1 M KOH are presented in Figure 2, data for composite **1** and **2** are also shown for comparison. Well-defined oxygen reduction reaction (ORR) peaks were observed at approximately –0.495, –0.568, and –0.451 V versus a saturated calomel reference electrode (SCE), for composites **1**, **2**, and **3**, respectively. The highest reduction current density of 0.0058 A cm<sup>-2</sup> was obtained for composite **3**. This indicates that in addition to a low carbon content and the lowest BET surface area, composite **3** also has the highest electrocatalytic activity for the ORR among all of the prepared composites. It is important to note that pure LAGP exhibits electrocatalytic activity towards the ORR,<sup>[9]</sup> and LAGP also displays high ionic conductivity. The existence of cavities and tunnels in the structure of LAGP accommodates gaseous oxygen molecules and



**Figure 2.** CV curves of composite **1** (—), composite **2** (---), and composite **3** (····) in 0.1 M KOH at 25 °C and a scan rate of 5 mV min<sup>-1</sup>.

[a] Dr. P. Kichambare, Dr. S. Rodrigues

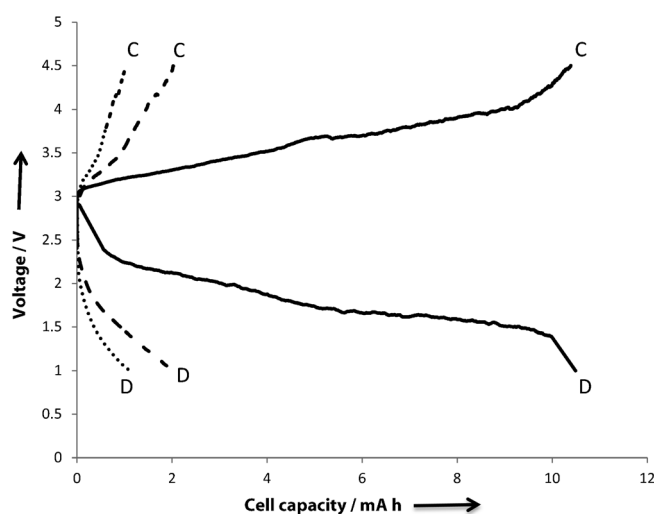
Aerospace Systems Directorate, Air Force Research Laboratory  
Wright-Patterson Air Force Base, Ohio 45433-7252 (USA)

E-mail: Padmakar.Kichambare@wpafb.af.mil

Supporting Information for this article is available on the WWW under  
<http://dx.doi.org/10.1002/ente.201200028>.

aids the diffusion and reduction of oxygen at the cathode. LAGP could also aid in stretching the oxygen molecules, facilitating dissociation, while the N–C blend enhances the electronic conduction. Therefore, the combination of a N–C blend and LAGP in composite **3** affords highly active electrocatalytic sites, enhanced electronic and ionic conductivity, and potential stretching of the oxygen molecule, which together lead to enhanced electrocatalytic performance. Based on the high surface area of composite **3**, its mesoporous structure, and electrocatalytic activity towards oxygen reduction, a solid-state lithium–oxygen cell with a 2 cm<sup>2</sup> area was fabricated in the form of a coin cell. The cathodic side of the cell contained perforations so that oxygen could access the cathode. The lithium anode was coupled to an oxygen cathode through a solid electrolyte laminate, as described in our previous work.<sup>[6]</sup>

The charge–discharge profiles of the lithium–oxygen cell containing the composite **3** cathode, at various current rates, are shown in Figure 3. This cell was reversibly charged and discharged using currents of 0.2, 1, and 5 mA in an oxygen atmosphere at 75 °C. The open circuit voltages (OCV) of the lithium–oxygen cells fabricated with composites **1**, **2**, and **3** were 3.03, 2.92, and 2.91 V, respectively. The difference in OCV is likely because of internal series resistances between various cell components as well as activation polarization of the cathode. Solid-state cells fabricated with composite **3** exhibited reproducible charge–discharge characteristics. To stabilize the cells after fabrication, these cells were subjected to a conditioning cycle that used a small discharge and charge current of 0.05 mA. During this conditioning process, we observed minor transient behavior (voltage fluctuation) in some of the cells. This may be attributed to the existence of interfacial flaws during cell fabrication. As can be seen in Figure 3, a lithium–oxygen cell containing composite **3** delivered a high discharge cell capacity of 10.5 mAh at a discharge current of 0.2 mA. At higher discharge currents of 1 mA and



**Figure 3.** The charge–discharge profiles for a lithium–oxygen cell using composite **3** as the cathode at discharge (D) and charge (C) currents of 5 mA (·····), 1 mA (----), and 0.2 mA (—).

2 mA, the cell capacity of the lithium–oxygen cells decreased. However, the cells constructed with composites **1** and **2** as the cathodes delivered 1.97 and 9.03 mAh discharge capacities, respectively, at a discharge current of 0.2 mA.<sup>[7]</sup> Discharge capacities of 1.44 and 0.7 mAh for cells containing cathodes composed of only the N–C blend or a C blend, respectively, have been reported previously.<sup>[8]</sup> Our results are consistent with those of Kumar et al.<sup>[6b]</sup>, who reported data for incremental increases up to 77 wt% LAGP in a cathode formulation (containing a mixture of Ketjenblack and Calgon activated carbon powder). These studies indicated that an increase in LAGP loading increased the discharge capacity of the cell. In addition, an increase in LAGP loading also increased the total weight of the cathode and lowered the energy density of the cells. Thus, there is a compromise between the wt% of LAGP loading and the discharge cell capacity/energy density of the cell. Our efforts were aimed at achieving a higher cell capacity with a lower wt% of LAGP in the cathode formulation. The energy densities, normalized with the weight of the cathodes, for composites **1**, **2**, and **3** were found to be 891, 3714, and 4361 Whkg<sup>-1</sup>, respectively, at a discharge current of 0.2 mA. In the present work, the energy density of the cathode containing composite **3** represents a nearly 1.2-fold improvement compared to the energy density for composite **2**. Compared to the cathode composed with only the N–C blend, the cell with composite **3** has a cell capacity seven times greater. This enhancement in cell capacity is because of improved electrocatalytic activity, the high mesoporosity of composite **3**, and the fast lithium ion conduction deep inside the cathode. All of the characteristics of composite **3** are indicative of highly active electrocatalytic sites that can catalyze discharge reactions. In addition, a higher cathode porosity increases oxygen diffusivity throughout the cathode and increases accumulation of reaction products that help to improve the cell capacity. It is reported that pores of different sizes are filled with discharge products at different rates<sup>[10]</sup> until the oxygen electrodes cease functioning. Figure 3 also shows that there was a significant potential drop during the initial stage of discharge due to both an activation barrier of cathode chemistry that includes sluggish kinetics, and series resistances between various cell components.

In summary, this work demonstrates superior cell performance of lithium–oxygen cells with cathodes that are formed from a new material, composite **3** (a N–C blend and 20 wt% LAGP). The discharge capacity of this cell is 10.5 mAh, which is an order of magnitude higher than with a mesoporous carbon cathode. This work indicates the potential of composite **3** as a promising and low-cost cathode material for lithium–oxygen batteries.

## Experimental Section

### Fabrication of oxygen cathode

The working cathode, composite **3**, was prepared from a mixture of a N–C blend and 20 wt% LAGP (composites **1** and **2** con-

tained 5 and 10 wt% LAGP, respectively). The N–C blend was prepared from a mixture of nitrogen-doped Ketjenblack (N–KB) and nitrogen-doped Calgon activated carbon (N–CA) in a 40:60 wt% ratio. The N–C and LAGP powders were ball-milled with a polytetrafluoroethylene (PTFE) suspension and mixed with deionized water to obtain a soft mass. The solid pastes were spread onto nickel foams and pressed by sandwiching between two stainless-steel plates at 1 MPa. The cathode specimens were dried overnight at 100 °C under vacuum. Solid-state lithium–oxygen cells with a 2 cm<sup>2</sup> area were fabricated by using commercially available cell casing under a dry argon atmosphere. Each cell consisted of a composite film mounted onto a nickel foam that acted as the working cathode, lithium metal was used as the anode, and polymer-coated LAGP acted as the electrolyte.

### Physical and electrochemical characterization

The morphology of the composite **3** powder was examined by using SEM. The BET surface area of composite **3** (Figure S1, see the Supporting Information) was obtained by using a nitrogen sorption instrument (Micromeritics ASAP 2020). The porosity of the cathode material was measured by using a gas pycnometer (Micromeritics, Accu Pyc II 1340). CV measurements were performed in a standard three-electrode cell configuration with 0.1 M KOH as the electrolyte, the CVs were measured at 25 °C with a scan rate of 5 mVmin<sup>-1</sup> by using a VersaSTAT 4 (Princeton Applied Research) electrochemical workstation. A paste that consisted of the N–C blend, 20 wt% LAGP, and Nafion (tetrafluoroethylene based fluoropolymer-copolymer) solution was prepared and spread onto the tip of a graphite rod, which was used as the working electrode. A Pt wire was used as the counter electrode and a SCE was used as the reference. The electrochemical performance of the solid-state lithium–oxygen cells fabricated with composite **3** was examined by using a computer-controlled VersaSTAT 4 electrochemical workstation. Charge–discharge measurements on these cells were performed in galvanostatic mode, and all measurements were performed under an oxygen atmosphere.

### Acknowledgements

This research was supported by the Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio. We thank Dr. B. Kumar at the University of Dayton Research Institute, Dayton, Ohio, for supplying the LAGP powder for this research work.

**Keywords:** batteries • carbon • glasses • mesoporous materials • oxygen reduction

- [1] P. G. Bruce, S. A. Freunberger, L. J. Hardwick, J.-M. Tarascon, *Nat. Mater.* **2012**, *11*, 19–29.
- [2] *Handbook of Batteries and Fuel Cells*, 2nd ed., (Ed.: D. Linden), McGraw-Hill, New York, **1984**, chap. 38.
- [3] a) G. Girishkumar, B. McCloskey, A. C. Luntz, S. Swanson, W. J. Wilcke, *J. Phys. Chem. Lett.* **2010**, *1*, 2193–2203; b) Y. Shao, S. Park, J. Xiao, J.-G. Zhang, Y. Wang, J. Liu, *ACS Catal.* **2012**, *2*, 844–857; c) R. Younesi, M. Hahlin, F. Bjorefors, P. Johansson, K. Edstrom, *Chem. Mater.* **2013**, *25*, 77–84.
- [4] K. M. Abraham, Z. Jiang, *J. Electrochem. Soc.* **1996**, *143*, 1–5.
- [5] a) H.-G. Jung, J. Hassoun, J.-B. Park, Y.-K. Sun, B. Scrosati, *Nat. Chem.* **2012**, *4*, 579–585; b) Z. Peng, S. A. Freunberger, Y. Chen, P. G. Bruce, *Science* **2012**, *337*, 563–566; c) H. Kitaura, H. Zhou, *Energy Environ. Sci.* **2012**, *5*, 9077–9084; d) Y. L. Li, J. J. Wang, X. F. Li, D. S. Geng, M. N. Banis, R. Y. Li, X. L. Sun, *Electrochem. Commun.* **2012**, *18*, 12–15; e) S. H. Oh, L. F. Nazar, *Adv. Energy Mater.* **2012**, *2*, 903–910; f) J. R. Harding, Y.-C. Lu, Y. Tsukada, Y. Sharo-Horn, *Phys. Chem. Chem. Phys.* **2012**, *14*, 10540–10546.
- [6] a) B. Kumar, J. Kumar, R. Leese, J. P. Fellner, S. J. Rodrigues, K. M. Abraham, *J. Electrochem. Soc.* **2010**, *157*, A50–A54; b) B. Kumar, J. Kumar, *J. Electrochem. Soc.* **2010**, *157*, A611–A616.
- [7] P. Kichambare, S. Rodrigues, J. Kumar, *ACS Appl. Mater. Interfaces* **2012**, *4*, 49–52.
- [8] P. Kichambare, J. Kumar, S. Rodrigues, B. Kumar, *J. Power Sources* **2011**, *196*, 3310–3316.
- [9] B. Kumar, P. Kichambare, S. Rodrigues, J. Kumar, R. G. Keil, *Electrochem. Solid-State Lett.* **2011**, *14*, A97–A99.
- [10] C. Trans, X. Q. Yang, D. Qu, *J. Power Sources* **2010**, *195*, 2057–2063.

Received: October 17, 2012

Revised: January 10, 2013

Published online on March 18, 2013