Hierarchically Porous Graphene as a Lithium−Air Battery Electrode

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ABSTRACT: The lithium−air battery is one of the most promising technologies among various electrochemical energy storage systems. We demonstrate that a novel air electrode consisting of an unusual hierarchical arrangement of functionalized graphene sheets (with no catalyst) delivers an exceptionally high capacity of 15000 mAh/g in lithium−O2 batteries which is the highest value ever reported in this field. This excellent performance is attributed to the unique bimodal porous structure of the electrode which consists of microporous channels facilitating rapid O2 diffusion while the highly connected nanoscale pores provide a high density of reactive sites for Li−O2 reactions. Further, we show that the defects and functional groups on graphene favor the formation of isolated nanosized Li2O2 particles and help prevent air blocking in the air electrode. The hierarchically ordered porous structure in bulk graphene enables its practical applications by promoting accessibility to most graphene sheets in this structure.

KEYWORDS: Li−air battery, graphene, specific energy, Li2O2, O2 reduction

Lithium-ion batteries have been widely used in many electronic devices that are important to our daily life. However, after a steady improvement of ∼10−15% during the last two decades, the energy density of lithium-ion batteries is now approaching its theoretical limit set by the energies of cathode and anode materials used in these batteries.† Therefore, in recent years, the pursuit of the next generation of energy storage systems has been intense globally.† Among various electrochemical energy storage systems explored to date, the lithium−air (Li−air) battery is one of the most promising technologies, with a theoretical energy density nearly 10 times that of conventional lithium-ion batteries.5−7 This is because lithium metal as an anode has a capacity 10 times higher than that of conventional graphite anodes, and oxygen as the cathode of a Li−air battery can be absorbed freely from the environment leading to a significant reduction in the weight and the cost of the battery.

The performance of Li−air batteries is affected by many factors such as relative humidity,8 oxygen partial pressure,9 choice of catalysts,10 electrolyte composition,11 the macrostructure of the air electrode,12,13 the micro- to nanostructure of carbonaceous materials,14 and overall cell designs.8,15 Precipitation of reaction products (such as Li2O2) on the carbonaceous electrode eventually blocks the oxygen pathway and limits the capacity of the Li−air batteries. Therefore, there is a critical need to design an optimum air electrode containing micrometer-sized open porosity for rapid oxygen diffusion and substantial nanoporosity (2−50 nm) to catalyze Li−O2 reactions while preventing excessive growth of the discharge products that block chemical pathways.

In this work, we use a colloidal microemulsion approach and demonstrate, for the first time, the construction of hierarchically porous air electrodes with functionalized graphene sheets (FGSs) that contain lattice defects and hydroxyl, epoxy, and carboxyl groups.16 Figure 1 shows the schematic structure of functionalized graphene16 with an ideal bimodal porous structure which is highly desirable for Li−O2 battery operation. Although graphene sheets and composites have been studied as electrode materials for Li−ion batteries,17−19 they typically form a two-dimensional (2D) layered structure that is not suitable for Li−air battery application. On the contrary, the three-dimensional (3D) air electrodes developed in this work consist of interconnected pore channels on both the micro- and nanometer length scales. High capacities of these air electrodes have been correlated with their bimodal pore structures. Further, modeling by density functional theory (DFT) and electron microscopy characterization suggests that lattice defect sites on the functionalized graphene play a critical role in the formation of small, nanometer-sized discharge products (Li2O2). The combination of the hierarchical pore structure and the effect of the defects during the discharge process produces an exceptionally high capacity of 15000 mAh/g, which is the highest value ever reported in this field.

Morphology of As-Prepared Graphene-Based Air Electrodes. Graphene and graphene-based composites have been studied as electrode materials for supercapacitors,17 Li-ion

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batteries,\textsuperscript{18} and proton-exchange membranes for fuel cells (PEM).\textsuperscript{19} In almost all these studies, the graphene sheets readily restack due to either van der Waals or capillary forces and form 2D structures that hinder the rapid gas diffusion that is essential for the efficient operation of Li-air batteries.\textsuperscript{20} Our work reveals for the first time that FGSs, if manipulated appropriately, can self-assemble into highly porous, 3D architectures with interconnected pore channels. These architectures are not only useful for Li/C\O{2} air batteries but also important for many other energy storage, conversion, and catalytic applications.

FGS used in this study was produced by the thermal expansion and simultaneous reduction of graphite oxide.\textsuperscript{21,22} While graphite oxide has a C/O ratio of \(\sim 2\), after thermal reduction at 1050 °C for 30 s, the C/O ratio of the FGS increases to \(\sim 15\) as a result of CO\textsubscript{2} release. With longer residence times, this ratio can be increased to values as high as \(\sim 300\). With the release of CO\textsubscript{2}, lattice defects form. The degree of defect formation and surface functionalization on the graphene sheets correlates with the C/O ratio.\textsuperscript{21–24} The C/O ratio reflects the relative content of the lattice defects and/or oxygen functional groups on the graphene sheets. The smaller the C/O ratio, the higher the number of functional groups/lattice defects on the FGS. When the C/O ratio increases from 15 to 100, the electrical conductivity of pellets produced with FGS also increases by approximately 2-fold from \(\sim 10^{4}\) to \(2 \times 10^{4}\) S/m (see supplementary Figure S1, Supporting Information).

To produce the FGS-based air electrodes, FGS was first dispersed in a microemulsion solution which also contained the binder materials (DuPont Teflon PTFE-TE3859 fluoropolymer resin aqueous dispersion, 60 wt % solids) for the electrode. After casting and drying, very unusual morphologies were produced as shown in panels a and b of Figure 2. Surprisingly, FGSs aggregated into loosely packed, “broken egg” structures leaving large interconnected tunnels that continue through the entire electrode depth (Figure 2a). These tunnels can function as numerous arteries that continuously supply oxygen into the interior of the electrode during the discharge process. More importantly, the complex pore structure is retained after electrolyte infiltration, unlike other porous carbon materials tested. Higher magnification observation of the “shells” of the “broken eggs” (Figure 2b) reveals that the “shells” consist of numerous smaller nanoscale pores contiguous with the large tunnels. This unique morphology is an ideal design for an air electrode. During discharge the robust large tunnels can function as “highways” to supply the oxygen to the interior parts of air electrode while the small pores on the walls are the “exits” which provide triphase (solid—liquid—gas) regions required for oxygen reduction.\textsuperscript{8,9,12}

The formation of this unique and useful FGS morphology results from the mixing step in which an aqueous poly(tetrafluoroethylene) (PTFE) microemulsion is added to the FGSs. Significant foaming occurs during mixing, resulting in a

\[
2\text{Li}^+ + \text{O}_2 + 2\text{e}^- \rightarrow \text{Li}_2\text{O}_2
\]

\[\text{Figure 1. Schematic structure of a functionalized graphene sheet (upper image) with an ideal bimodal porous structure (lower image) which is highly desirable for Li–O}_2\text{ battery operation. Functional groups and lattice defects on FGSs showing epoxy and hydroxyl groups on both sides of the graphene plane, carboxyl, and hydroxyl groups at the edges, a 5–8–5 defect (yellow), and a 5–7–7–5 (Stone–Wales) defect (blue). Carbon atoms are gray, oxygen atoms are red, and hydrogen atoms are white.}\]
distribution of bubble sizes ranging in diameter from tens of nanometers to tens of micrometers (see supplementary Figure S2, Supporting Information). In many cases the large bubbles contain numerous smaller-diameter bubbles. The hydrophobic nature of the FGS surfaces forces the particles to assemble in the surfactant-rich “skin” of each bubble. Upon drying, the FGS forms a carbonaceous replica of the foam, resulting in the final interconnected structure containing large tunnels and small pores. FGS has not only a unique 2D macromolecular structure but also a hydrophobic plane (when its C/O > 10) which enables pores. FGS has not only a unique 2D macromolecular structure with a H3 hysteresis loop according to the IUPAC classification (Figure S3, Supporting Information). In many cases the large bubbles contain numerous smaller-diameter bubbles. The hydrophobic nature of the FGS surfaces forces the particles to assemble in the surfactant-rich “skin” of each bubble. Upon drying, the FGS forms a carbonaceous replica of the foam, resulting in the final interconnected structure containing large tunnels and small pores. FGS has not only a unique 2D macromolecular structure but also a hydrophobic plane (when its C/O > 10) which enables pores. FGS has not only a unique 2D macromolecular structure with a H3 hysteresis loop according to the IUPAC classification.

Earlier, we applied the same approach on Ketjenblack (KB) carbon (EC-600JD, Nobel Polymer Chemicals, Chicago, IL). Alternatively, the morphologies of the KB-based air electrode are quite different from the graphene ones even when we use the same preparation approach. Since porous KB has a much larger particle size than that of the molecularly thin graphene sheets, most of the PTFE microemulsion is absorbed into the pores instead of interacting with carbonaceous material on the interface of the bubbles. Accordingly, the discharge capacity of the KB-based air electrode is much lower than that of FGS-based air electrode.

The N2 adsorption isotherm and the BJH pore size distribution are shown in Figure S3 (Supporting Information). The N2 adsorption isotherm of the FGS electrode shows a type II curve with a H3 hysteresis loop according to the IUPAC classification. The absence of saturation at unity pressure on the adsorption curve shows the presence of macro pores larger than 100 nm. The hysteresis in the middle pressure range suggests the existence of slit-type meso- or nanoporosity typically formed by aggregates of platelike particles. The microporosity is not analyzed here. The size in the hysteresis loop is related to the mesopore volume and the connectivity of the pores. The BJH pore size distribution, although not accurate for this type of complex pore geometries, does show the continuous presence of a wide range of porosity from nanometer to a few hundred nanometer scales. The average pore size calculated from Figure S3 (Supporting Information) is about 18 nm, within the pore-size range typically found in a high-capacity air electrode. The pore volume and surface area of the air electrode are 0.84 cm³/g and 186 m²/g, respectively. The surface area of the electrode decreased from the FGS powder (590 m²/g) because of the addition of Teflon binder.

The processing method described above was used to prepare the air electrodes with FGSs of two different C/O ratios (14 and 100) resulting in similar final morphologies (see supplementary Figure S4 in the Supporting Information for the morphology of the air electrode consisting of FGS with C/O = 100). Although the overall cathode structures were alike, the morphologies of the reaction products that formed during discharge on the two surfaces were quite different. Panels c and d of Figure 2 compare the surface morphologies of the discharged air electrodes using graphene with C/O = 14 and 100, respectively. In both cases, the primary discharge product formed on the graphene surfaces was Li₂O₂ as confirmed by X-ray diffraction (XRD) (see supplementary Figure S5, Supporting Information) and selected area electron diffraction (SAED) (Figure 2f) of the particles (~10 nm) on FGS (C/O = 14) shown in the higher magnification transmission electron microscopy (TEM) image of Figure 2e. Unlike conventional carbonaceous electrodes in which a dense, thick layer of large Li₂O₂ particles is typically formed on the electrode surface, the Li₂O₂ particles deposited on FGS are nanometer-sized and isolated (panels c, d, and e of Figure 2).

There is no evidence of large particle formation that blocks the air channels. Further observation showed that the deposited Li₂O₂ particles were consistently smaller on the graphene with a lower C/O ratio (C/O = 14) than FGS with a higher C/O ratio (C/O = 100). Figure 2d also shows fewer Li₂O₂ particles in the air electrode made from FGS with C/O = 100, with a corresponding increase in size and spacing between precipitates. These observations suggest that differences in Li₂O₂ nucleation and growth are likely related to the lattice defects and/or functional groups, existing on the different FGSs as discussed later in this work.

To further verify the utility of the hierarchical pore organization, we also prepared a “paper-like” FGS electrode by filtration of an FGS dispersion and tested it as an air electrode under identical conditions. During evaporative drying of the filtered material, capillary forces restack the high-aspect-ratio graphene sheets and form 2D electrode structures that severely inhibit oxygen and electrolyte diffusion. (See supplementary Figure S6 in the Supporting Information.) Such cathodes had capacities of only less than 100 mAh/g, providing further support for the unique aspects of the hierarchical and contiguous pore organization to achieve the observed electrochemical performance with these FGS materials.

Electrochemical Performance of Li–Air Batteries Using Graphene Electrodes. Figure 3a shows the discharge curve of a Li–O₂ cell utilizing an air electrode prepared with FGS of C/O = 14 and tested in pure oxygen at an initial pressure of ~2 atm (the pressure will decrease during discharge because of oxygen consumption). Surprisingly, the discharge capacity reaches 15000 mAh/g carbon with a plateau at around 2.7 V. The corresponding specific energy is 39714 Wh/kg carbon, giving an average voltage of 2.65 V. This is the highest capacity reported to date for nonaqueous Li–O₂ batteries. These results are highly repeatable with multiple parallel test results showing similar capacity under the same test conditions. To exclude possible electrochemical contributions from the decomposition of organic functional groups on the graphene sheets, the electrode produced with the FGS paper was also discharged to 2.0 V in pure argon as shown in Figure 3b. Clearly, any capacity contribution arising from the functional groups can be ignored (<40 mAh/g) within the voltage range in this work. To minimize the electrolyte decomposition as observed in Li–O₂ batteries when carbonate solvent based electrolytes were used, ether-based electrolyte (LiTFSI in tri(ethylene glycol) dimethyl ether (Triglyme)) was used in this work. As discussed above, a significant amount of Li₂O₂ has been observed (see Figure S52 in the Supporting Information and Figure 2f), which is consistent with the formation of Li₂O₂ by other groups when ether-based electrolytes were used in Li–O₂ cells. To further evaluate their potential for practical application, Li–air batteries were tested in a pouch-type cell configuration (see inset of Figure 3c) in which the polymeric pouch was used to regulate O₂ and H₂O ingress. The pouch cell was operated in the ambient environment with an oxygen partial pressure of 0.21 atm and 20% relative humidity. The resulting discharge curve for the cell is shown in Figure 3c. At the same current density of 0.1 mA/cm², the specific capacity based on the carbon weight exceeded 5000 mAh/g. This further confirms the unique contribution of the hierarchical pore structure on performance. Other possible contributions to the unprecedented performance include (i) the superior electronic conductivity of graphene and (ii) the appropriate choice of a nonaqueous based electrolyte.
Figure 3d shows the discharge curve measured on Li–O₂ batteries using FGS as the air electrodes. (a) The discharge curve of a Li–O₂ cell using FGS (C/O = 14) as the air electrode (Pₐₒ₂ = 2 atm). (b) The same Li–O₂ cell as in (a) but tested in the pure argon atmosphere. (c) Discharge curve of a pouch-type Li–air cell made from FGS (C/O = 14) operated in ambient environment (Pₐₒ₂ = 0.21 atm, relative humidity = 20%). The inset shows the prototype of the pouch cell. (d) The discharge curve of a Li–O₂ cell using FGS (C/O = 100) as the air electrode (Pₐₒ₂ = 2 atm).

Table 1. DFT Calculated Binding Energies of (Li₂O₂)ₙ Clusters on the Perfect and the 5–8–5 Defect Graphene Surfaces with Functional (CCOH) Group

<table>
<thead>
<tr>
<th>binding energy, Eᵇ (eV)</th>
<th>cluster</th>
<th>perfect graphene</th>
<th>5–8–5 defect graphene</th>
<th>5–8–5 defect graphene with COOH group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂O₂</td>
<td>−0.26</td>
<td>−0.70</td>
<td>−0.90</td>
<td></td>
</tr>
<tr>
<td>(Li₂O₂)₂</td>
<td>−1.15</td>
<td>−1.27</td>
<td>−0.82</td>
<td></td>
</tr>
<tr>
<td>(Li₂O₂)₃</td>
<td>−1.60</td>
<td>−1.77</td>
<td>−0.90</td>
<td></td>
</tr>
<tr>
<td>(Li₂O₂)₆</td>
<td>−1.85</td>
<td>−2.08</td>
<td>−1.18</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3d shows the discharge curve measured on Li–O₂ batteries with cathodes fabricated from FGS with a C/O ratio of 100 (C/O = 100). The capacity delivered from FGS with reduced defect/functional group concentrations is approximately one-half that of cathodes synthesized from FGS with greater number density of combined lattice defects and the functional sites (C/O = 14, Figure 3a). This finding is consistent with the observed Li₂O₂ particle densities observed in the scanning electron microscopy (SEM) and TEM images shown in panels c and d of Figure 1 and is further supported by the DFT modeling presented below. Preferred growth, or aggregation, of Li₂O₂ on defect regions of the FGS (defects) is further investigated in the following section.

Deposition Mechanism of Li₂O₂ on the Graphene Surface.

To better understand the deposition mechanism of Li₂O₂ particles on FGS during discharge on the molecular level, periodic DFT calculations were performed using the Vienna ab initio simulation package (VASP).³⁷,³⁸ To account for the possible effects induced by the defect sites on the FGS, we calculated the interactions of various sizes of Li₂O₂ clusters on the graphene substrate with a 5–8–5 defect site. To account for possible functionalized groups on the graphene sheet, we also calculated, as an example, the interactions of adsorbed (Li₂O₂)ₙ clusters on the 5–8–5 defect graphene substrate with a pre-existing COOH group. The interaction (binding) energies between the (Li₂O₂)ₙ cluster and the supported graphene surfaces calculated from DFT are summarized in Table 1, and the corresponding optimized structures of (Li₂O₂)ₙ cluster/graphene are shown in Figure 4. Calculations were also performed on other defect structures and functional groups with similar findings, and the results are not included here due to space limitations.

The DFT results show only weak interactions between the Li₂O₂ monomer and graphene substrate, similar to a physical adsorption mechanism. The calculated binding energy of the Li₂O₂ monomer is only −0.26 eV (Table 1). However, this interaction becomes much stronger (−0.70 eV) if the Li₂O₂ monomer binds at the vicinity of a 5–8–5 defect site on the graphene surface (−0.7 eV), and even stronger on COOH groups associated with the defects (−0.9 eV), indicating that the Li₂O₂ particles most likely prefer to nucleate and grow around the defective sites with functional groups in FGS. With increasing (Li₂O₂)ₙ cluster size, the binding energy between the Li₂O₂ nanocluster and the FGS generally increases. Since the binding energy is related to the stability of the earlier nuclei on the surface, the theoretical findings suggest that the cathode structure can be optimized by tailoring the number and positions of the defects and functional groups on the graphene. Because we only tackle the very beginning stage of nucleation, the structure of the formed Li₂O₂ particle (up to Li₁₂O₁₂) is amorphous. As shown in Figure 4, the preferred growth mode, however, is most likely 2D (flatly covering the graphene support) instead of 3D. After the nucleation, the most exposed surface orientation of the Li₂O₂ particle is the (100) structure.³⁹
To further describe the system, an aggregation model patterned after the work of Mei et al.\textsuperscript{40} was applied to the Li$_2$O$_2$–graphene composite. Here, we simulate the Li$_2$O$_2$ aggregation process on the graphene surface as a reaction of an adsorbed Li$_2$O$_2$ monomer with an existing $(\text{Li}_2\text{O}_2)^n$/C$_0$ ($n \geq 2$) cluster:

$$[\text{Li}_2\text{O}_2]^n_{/C_0} + \text{Li}_2\text{O}_2 \rightarrow (\text{Li}_2\text{O}_2)^n_{/C_0}$$

The driving force for this aggregation process is then represented by the free energy change

$$\Delta G = G(\text{Li}_2\text{O}_2)^n_{/C_0} - G(\text{Li}_2\text{O}_2)^{n-1}_{/C_0} - G_{\text{Li}_2\text{O}_2}$$

Assuming the $\Delta(TS)$ and $\Delta(PV)$ terms (where $T$ is the temperature, $S$ is the entropy, $P$ is the pressure, and $V$ is the volume) have negligible contribution to the free energy change because of the condensed phases involved, $\Delta G$ can be calculated using the following equation

$$\Delta G = E^b_{(\text{Li}_2\text{O}_2)^n_{/C_0}} - E^b_{(\text{Li}_2\text{O}_2)^{n-1}_{/C_0}} - E^b_{\text{Li}_2\text{O}_2}$$

A negative value of $\Delta G$ indicates an energetically favorable process. As indicated in eq 3, the aggregation process depends upon the binding energy of an isolated Li$_2$O$_2$ monomer. Figure 5 shows the free energy changes of Li$_2$O$_2$ aggregation on both defect-free and 5–8–5 defect graphene surfaces with and without pre-existent COOH surface groups. For the pristine graphene surface, the aggregation of adsorbed Li$_2$O$_2$ monomers is energetically favorable until the formation of $(\text{Li}_2\text{O}_2)^5$ clusters,

while further aggregation to the larger $(\text{Li}_2\text{O}_2)^n$ ($n > S$) becomes energetically unfavorable. This is due to the fact that the interaction between the Li$_2$O$_2$ monomer and the perfect
Li₂O₂ particles are observed (Figure 2d) and the particle size distribution is less homogeneous. The larger particles in Figure 2d could result from Li₂O₂ cluster aggregation on the graphene surface. Such structure control could be highly advantageous from the DEF calculations. More detailed studies using a combination of electrochemical and theoretical approaches are needed to further understand the functions of the defects.

In summary, primary Li-air batteries containing hierarchically porous FGS deliver an extremely high capacity of 15000 mAh/g, highlighting the potential application of graphene in the metal-air system. This electrode design also shines light on how to control the architecture and surface chemistry of the carbon electrode for rechargeable Li-O₂ batteries. Two critical factors are responsible for the significantly improved performance of the graphene-based air electrode. One is the unique morphology of the graphene-based air electrode in which numerous large tunnels facilitate continuous oxygen flow into the air electrode while other small “pores” provide ideal triphase regions for the oxygen reduction. Another important factor is related to the Li₂O₂ deposition mechanism on the graphene surface. DFT calculations show that Li₂O₂ prefers to nucleate and grow near functionalized lattice defect sites on graphene with functional groups as a result of the relatively stronger interaction between the deposited Li₂O₂ monomer at the 5−8−5 defects. Most importantly, consistent with the experiments, the changes in free energy as a function of the size of Li₂O₂ cluster suggest that in the vicinity of those defective sites the aggregation of Li₂O₂ clusters is energetically unfavorable; therefore the deposited Li₂O₂ would form the isolated nanosized “islands” on FGS, further ensuring smooth oxygen transport during the discharge process. Limited size or thickness of the reaction products with preferred growth points may also improve the rechargeability of Li-air batteries because it prevents continuous increase in electrode impedance and provides better access for a catalyst during the charging process.

**Methods. Air Electrode Preparation.** The air electrode was prepared by a dry rolling process described in our previous work. Functionalized graphene sheets were provided by Vorbeck Materials Corp., Jessup, MD, USA (under the trade name of Vor-x) and contain lattice defects and oxygen (epoxy, hydroxyl, and carboxyl) functional groups with an approximate C/O ratio of 14 or 100. In as-produced form, FGS contains approximately 80% single-sheet graphene along with stacked graphene (graphene stacks) as described previously. The weight ratio between FGS (or Vor-x) and PTFE binder was controlled at 75:25. The final loading of graphene in the electrode was 2.1 mg/cm². The thickness of the graphene-based air electrode was 0.035 cm. To investigate the hierarchical porosity effect in a graphene-based air electrode, a paper-like FGS electrode was also prepared by a filtration method for comparison. In this case FGS (~10 mg) and cetyl trimethylammonium bromide (CTAB, 0.2 g) were added into 10 mL water and sonicated for 30 min to form a homogeneous suspension. Then the suspension (1 mL) was filtered, washed with ethanol, and dried in ambient conditions. The graphene film was peeled off the membrane and used directly as the air electrode.

**Physical Characterization.** The structure of the discharged products was characterized by using a Philips X'Pert X-ray diffractometer in a θ–2θ scan mode and Cu Ka radiation at λ = 1.54 Å. The discharged graphene-based air electrode was scanned at 2°/min between 10 and 80°. A JEOL 5900 SEM equipped with a Robinson series 8.6 backscattered electron detector and an EDAX Genesis energy-dispersive spectroscopy (EDS) system with a Si (Li) EDS detector was used to investigate the particle morphology. The optical microscope images were taken by using a Meiji metallurgical microscope (model MX8530) with a physical characterization.
The theoretical energy density of Li–air batteries.

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