Ultrahigh Capacity Lithium-Oxygen Batteries Enabled by Dry-Pressed 
Holey Graphene Air Cathodes

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Abstract

Lithium-oxygen (Li-O\textsubscript{2}) batteries have the highest theoretical energy density of all the Li-based energy storage systems, but many challenges prevent them from practical use. A major obstacle is the sluggish performance of the air cathode, where both oxygen reduction (discharge) and oxygen evolution (charge) reactions occur. Recently there have been significant advances in the development of graphene-based air cathode materials with a large surface area and high catalytic activity for both oxygen reduction and evolution reactions. However, most studies reported so far have examined air cathodes with a limited areal mass loading rarely exceeding 1 mg/cm\textsuperscript{2}. Despite the high gravimetric capacity values achieved, therefore, the actual (areal) capacities of those batteries were far from sufficient for practical applications. Here, we present the fabrication, performance, and mechanistic investigations of high mass loading (up to 10 mg/cm\textsuperscript{2}) graphene-based air electrodes for high-performance Li-O\textsubscript{2} batteries. Such air electrodes could be easily prepared within minutes under solvent-free and binder-free conditions by compression molding holey graphene because of the unique dry compressibility of this graphene structural derivative with in-plane holes. High mass loading Li-O\textsubscript{2} batteries prepared in this manner exhibited excellent gravimetric capacity and thus ultrahigh areal capacity (as high as ~40 mAh/cm\textsuperscript{2}). The batteries were also cycled at a high curtailing areal capacity (2 mAh/cm\textsuperscript{2}), with ultrathick cathodes showing a better stability during cycling than thinner ones. Detailed postmortem analyses of the electrodes clearly revealed the battery failure mechanisms under both primary and secondary modes, which were the oxygen diffusion blockage and the catalytic site deactivation, respectively. The results strongly suggest that the dry-pressed holey graphene electrodes are a highly viable architectural platform for high capacity, high performance air cathodes in Li-O\textsubscript{2} batteries of practical significance.
1. Introduction

The demand for high performance energy storage systems is increasing in order to provide electrical energy for portable electronics, grid-scale applications, and electric transportation. Although performance requirements can vary significantly for these different applications, an ideal advanced battery system should, in general, have a small footprint (i.e., lightweight and small volume), high capacity, high energy density, good cyclability, high power/rate capability, and ensured safety. In electric transportation, lithium (Li) ion battery technology is currently being used in the electric vehicles (EVs), but their energy densities are intrinsically limited and insufficient for the need of more powerful future EVs.\(^1\)-\(^3\) In aeronautics, energy storage systems for future electric aircrafts will demand even higher energy densities.\(^4\)

Li-air batteries are an advanced Li-based energy storage system that utilize Li metal and oxygen (O\(_2\)) as the anode and cathode reactants, respectively.\(^1\)-\(^3\) Li metal has the highest energy density value among the solids (3860 mAh/g), while O\(_2\) is sustainable with an unlimited supply from the air. Thus, the Li-air battery system is expected to have an extraordinarily high theoretical energy density (11700 Wh/kg), which significantly surpasses that of typical Li ion battery systems (< 500 Wh/kg) and can potentially revolutionize the energy storage technology if successfully developed.\(^5\)

Li-O\(_2\) batteries using pure O\(_2\) atmosphere are the most widely studied Li-air batteries. However, many challenges remained to be addressed in order to advance their readiness level toward practical applications. In an ideal non-aqueous Li-O\(_2\) battery, the discharge reaction is an oxygen reduction reaction (ORR) involving the formation of lithium peroxide (Li\(_2\)O\(_2\)) from Li and O\(_2\). The charge reaction is an oxygen evolution reaction (OER), in which Li\(_2\)O\(_2\) decomposes into O\(_2\) and Li metal back to the anode surface. One of the major bottlenecks in Li-O\(_2\) battery technology has been the sluggish performance of air cathodes where ORR and OER occur.\(^6\),\(^7\)
Most of current research has focused on the development of cathode materials that can alleviate this problem, although some recent studies have also focused on other aspects such as the use of redox mediators as “soluble catalysts”. Carbon nanomaterials, such as carbon nanotubes and graphene, have received special attention as the air cathodes because of their low weight, high surface area, excellent electrical conductivity, and chemical stability. In addition, carbon nanomaterials are excellent catalytic substrates, which, upon heteroatomic doping, or incorporation of metal-containing catalysts, become even more effective in catalyzing ORR/OER reactions.

While significant progress has been made in the air cathode material development, very few studies have been devoted to the preparation of high capacity Li-O₂ batteries with energy densities that are practically meaningful. Carbon nanomaterial-based air cathode materials with reported ultrahigh gravimetric performance were often of very small areal loadings that rarely surpassed 1 mg/cm² with only very few exceptions (no more than ~2 mg/cm²). In a recent study, Zhou et al. reported an outstanding graphene-based air electrode material design with hierarchical porosity and controlled surface functionality. Such Li-O₂ cells exhibited a deep discharge capacity as high as 19800 mAh/g and were cycled 50 times with a curtailing capacity of 1000 mAh/g at a current density of 1000 mA/g. However, the areal loading of the active material was only 0.25 mg/cm². Thus, the true total and cyclable areal capacities are calculated to be ~5 and 0.25 mAh/cm², respectively. In comparison, the typical cyclable capacity of current commercial Li ion batteries is in the range of ~2 – 4 mAh/cm². Scaling up the air cathode for practical applications, therefore, requires significant increase in the electrode areal loading and thickness. Meanwhile, the desirable porous architecture needs to be retained to ensure the effectiveness of the battery reactions that are already intrinsically kinetically sluggish. It remains
unknown whether the reported ultrahigh gravimetric performances could still be achieved at high cathode mass loading.

While the cathode reactant is gaseous oxygen obtained from external atmosphere, the air cathode of a Li-O$_2$ battery is the true physical location for the battery reactions. Unlike their aqueous counterparts, non-aqueous Li-O$_2$ batteries often contain discharge products that are insoluble in the electrolyte.$^3$ In order to achieve high capacity, the cathode compartment needs sufficient space, i.e., pore size and volume, to host a large amount of solid discharge products. The total surface area of the cathode material, typically measured by gas adsorption/desorption, is less relevant in Li-O$_2$ batteries in comparison to other energy storage systems, such as supercapacitors.$^{39,40}$ To ensure rechargeability, the insoluble discharge products need to be attached to the conductive substrate for electrochemical decomposition during charging. Therefore, an ideal high capacity air electrode should have an optimized substrate-pore architecture to allow for the growth/filling of discharge products and the subsequent decomposition/emptying during charging while maintaining electrical contact at all time.

It was recently demonstrated in our laboratories that graphene-based articles of arbitrary shapes could be prepared via direct compression of holey graphene (hG) powder under solvent-free and additive-free conditions at room temperature.$^{41}$ The procedure was facilely conducted using a common pressing die and a hydraulic press, and could be completed within minutes in comparison to the typical lengthy multi-step procedure involving slurry preparation, solvent evaporation, and often the use of parasitic binders to prepare carbon-based electrodes. The hG material is the key to the procedure because the holes through the lateral surface of the graphene sheets allow air molecules to readily escape from the interstitial space between adjacent sheets during dry compression. Also, because of the presence of the in-plane holes that allow facile through-thickness mass transport, hG has been proven to be a superior electrode material to intact
graphene for supercapacitors,\textsuperscript{42,43} Li ion batteries,\textsuperscript{44,45} and Li-O\textsubscript{2} batteries.\textsuperscript{46} The dry compression properties of hG therefore provide a unique opportunity to facilely achieve binder-free graphene-based electrodes of ultrahigh areal loading with high performance. Indeed, supercapacitors using dry-pressed hG electrodes with areal loading as high as 30 mg/cm\textsuperscript{2} were achieved with little reduction in gravimetric performance even in comparison to devices with loadings as low as 1 mg/cm\textsuperscript{2}.\textsuperscript{41} With high mass loading, the devices exhibited outstanding areal capacitances of greater than 1 F/cm\textsuperscript{2}. It was also demonstrated that the hG powder could be used as the host matrix to fabricate complex electrode architectures with precise catalyst placements for Li-O\textsubscript{2} batteries using the dry compression approach.\textsuperscript{47}

Here, we report that the binder-free, dry-pressed hG discs with areal loadings as high as 10 mg/cm\textsuperscript{2} exhibited high performance as air cathodes for non-aqueous Li-O\textsubscript{2} batteries. These electrodes enabled ultrahigh areal capacity when operated in the primary (i.e., full discharge) mode. The thick hG electrodes were also operated in the secondary (i.e., rechargeable) mode at a high curtailing capacity and exhibited excellent cyclability. The postmortem analysis of thick electrodes was studied in great detail, and the mechanism for the progress of battery reactions in these high capacity Li-O\textsubscript{2} batteries was proposed.

2. Results and Discussion

2.1. Preparation of Dry-Pressed hG Air Cathodes

hG was prepared using a previously reported facile one-step controlled air oxidation process.\textsuperscript{43,48} The resultant hG sheet exhibited holes with diameters in the range of \(~5 \text{ – } 15\) nm throughout the lateral surface, as shown in a typical scanning electron microscopy (SEM) image in Figure 1a. For Li-O\textsubscript{2} batteries, the air cathodes were prepared using hG by a facile, dry compression molding process enabled by the unique compressibility of hG without the use of any
polymer binder or solvent. In the process, the as-produced hG powder was directly loaded in a pressing die and compressed at room temperature using a laboratory hydraulic press unit (Figure 1b). Two precisely-cut separation layers (such as glossy Celgard membrane discs) were used to encase the hG powder in order to prevent its adherence to the die surfaces. The separation layers were readily peeled off from the hG disc to form a free-standing electrode (Figure 1c). The air electrode was then incorporated into a Li-O₂ coin cell, in which a perforated cathode cap was used to allow for oxygen passage (Figure 1d; see details in Methods).

**Figure 1.** High capacity Li-O₂ batteries with dry-pressed holey graphene (hG) air cathodes. (a) A typical SEM image of a hG sheet. (b) A schematic drawing (not to scale) on using the hydraulic compression of hG powder to directly prepare hG air cathodes. (c) A photograph of dry-pressed hG air cathodes with stainless steel (SS) woven mesh support (left), with Al mesh support (middle), and freestanding (right). (d) A schematic drawing (not to scale) of a high capacity Li-O₂ coin cell battery with an ultrathick air cathode. (e-g) Side-view SEM images of an hG air cathode (mₐ ~ 10 mg/cm²) with SS woven mesh supports. Most hG sheets were horizontally aligned as shown in (f) and area 1 labeled in (e). However, compression from the interwoven SS wires resulted in different localized orientations of hG sheets, even those near vertical to external compression force as shown in (g) and area 2 labeled in (e).

When using perforated Al meshes as the separation layers, the top mesh could be left attached to serve as the current collector to ensure a good electrical contact, with perforation
allowing sufficient oxygen access (Figure 1c). As expected, higher compression pressure resulted in more compact hG sheet packing and higher density.\textsuperscript{41} At a compression pressure of 200 MPa (used in this work unless otherwise specified), the thicknesses of the hG discs for areal mass loadings ($m_A$) of 5 and 10 mg/cm$^2$ were ~50 and ~100 µm, respectively, as measured directly by a thickness gauge or SEM (Figure S1a in Supporting Information). The density values of these hG discs were therefore ~1 g/cm$^3$.

Air cathodes were also prepared by sandwiching the hG powder using two precisely cut stainless steel (SS) woven meshes as the support and current collector (Figures 1c & 1e-g). These electrode discs were thicker than those using flat separation layers because the ~150-µm thick SS wires were embedded in the architecture. hG sheets in the electrode discs with flat separation layers were horizontally aligned (Figure S1a and b in the Supporting Information). However, in a SS woven mesh-supported hG electrode disc, the intertwined SS wires caused the hG sheets to align in various orientations in the final architecture. The sheets were not only in the direction parallel to disc surfaces (Figure 1f), but also nearly vertically aligned at some locations (Figure 1g), the latter of which is the most preferred graphene sheet orientation for mass transport through the electrode thickness. The use of woven wire meshes was the key for such unique architecture, because the hG sheets compressed between two close-neighbord (< 100 µm in distance) SS wires became aligned more along the wire interfaces within the confined space than the direction of the external compression force (see area 2 in Figure 1e). Consistently, although air electrodes with different separation layers or support structures all performed well, those with sandwiching SS woven meshes provided the highest specific capacity per gram carbon at the same $m_A$ in similarly assembled Li-O$_2$ cells (Figure S1c in Supporting Information). Therefore, most hG air electrodes in this work used SS woven wire mesh supports unless otherwise specified. It is recognized, however, that the current SS woven meshes are much heavier than the
perforated Al meshes (~40 vs. 3 mg/cm²). For practical Li-O₂ cells, dry-pressed hG electrode support with similar interwoven wiring architecture but much lighter in material weight would be more desirable.

2.2. Full Discharge Properties

As shown in Figure 2a, the full discharge voltage profile for a Li-O₂ battery with a dry-pressed hG air cathode with \( m_A \) of 5 mg/cm² at an areal current density \( (I_A) \) of 0.1 mA/cm² was stable and flat during majority of the discharge time. The discharge potential measured at half total capacity \( (V_{C/2}) \) was ~2.74 V, with a discharge overpotential of only 0.22 V (considering \( E^0 = 2.96 \)V for the \( \text{Li}_2\text{O}_2 \)-based discharge reactions\(^3\)), suggesting good ORR properties of the packed hG materials in the air cathode. The discharge lasted more than 160 h, corresponding to a specific capacity \( (C_m) \) of ~7700 mAh/g and a specific energy \( (E_m) \) of ~21,000 Wh/kg. These weight-averaged values are on par with most graphene-based air cathodes reported (without additional catalyst), but the mass loadings used here are much higher (Table S1 & S2 in Supporting Information). As expected, increasing the current density to 0.2 and 0.5 mA/cm² resulted in decrease in specific capacity (6540 and 2824 mAh/g) and discharge potential (2.59 and 2.36 V). Because of the high mass loading, the cells exhibited outstanding areal capacities \( (C_A) \), which were calculated to be as high as 38, 33, and 14 mAh/cm² at 0.1, 0.2, and 0.5 mA/cm², respectively. Areal capacity is a critical parameter in the evaluations of practical batteries with large mass loadings. The \( C_A \) values calculated from most of the previous literature reports with carbon-based air electrodes rarely surpassed 10 mAh/cm² while the \( m_A \) values were usually smaller than 1 mg/cm² (Table S2).
At the same areal current density, varying the mass loading resulted in changes in specific capacity. As shown in Figures 2b and 2c, at 0.2 mA/cm², the hG air cathode with $m_A$ of 5 mg/cm² exhibited a higher specific capacity than those with either smaller or higher mass loadings. For example, the specific capacities of hG air cathodes with $m_A$ of 2, 5, and 10 mg/cm² were 3819, 6540, 3530 mAh/g, respectively (Figure 2b and Table S1 in the Supporting Information). The full discharge time (or total capacity) of the 10 mg/cm² electrode was ~12% higher than that of the 5 mg/cm² electrode under otherwise identical conditions (run side-by-side in the same oxygen chamber; Figure 2b inset). The two electrodes also exhibited almost identical discharge profiles up till ~150 h of discharge, when the cell with the 5 mg/cm² hG electrode started to fail while that with the 10 mg/cm² electrode was stable for another 20 h.
The above findings can be understood by considering two competing factors. First, at a constant areal current density $I_A$, the smaller the $m_A$, the higher the specific current density in terms of unit mass ($I_m$, in mA/g). $I_m$ has been very commonly used in the evaluations of low mass loading air electrodes.\textsuperscript{1-3} It is known that higher $I_m$ usually results in smaller total discharge capacity, reduced cyclability, and lower discharge potential. At $I_A$ of 0.2 mA/cm\textsuperscript{2}, the $I_m$ values for hG electrodes with $m_A$ of 2, 5, and 10 mg/cm\textsuperscript{2} were 100, 40, 20 mA/g, respectively. According to the data shown in Figure 2b, the $V_{C/2}$ values for these hG electrodes were 2.52, 2.59, and 2.67 V, respectively. Such $V_{C/2} - m_A$ dependence is consistent with the expected effect from the respective change of $I_m$. Second, it can be expected that higher $m_A$, or thicker electrodes, may exhibit reduced cathode material utilization efficiency across the entire thickness, especially considering the depth-wise concentration gradient of dissolved oxygen in the electrolyte. Consistent with this hypothesis is the finding that the areal capacity of hG air cathodes exhibited little increase beyond ~35 mAh/cm\textsuperscript{2} with $m_A \geq 5$ mg/cm\textsuperscript{2} at 0.2 mA/cm\textsuperscript{2} (Figure 2c). In other words, the entire thickness of a dry pressed hG air cathode can only be effectively utilized up to ~5 mg/cm\textsuperscript{2} (“thick” electrodes) under current deep discharge conditions.

To fully illustrate the discharge product distribution in the thick electrode configurations, multi-layered “analytical” hG air cathodes with extra Al mesh insertions were designed so that postmortem analyses of electrode materials at different depths could be conveniently identified, isolated and evaluated. In an analytical air cathode with the total hG mass loading of 7 mg/cm\textsuperscript{2} and one Al mesh insertion, the layered architecture from top (air side) to bottom (separator/Li side) was: SS wire mesh $\parallel$ 3.5mg/cm\textsuperscript{2} hG $\parallel$ Al mesh $\parallel$ 3.5 mg/cm\textsuperscript{2} hG $\parallel$ Al mesh. After full discharge (~21 mAh/cm\textsuperscript{2}), the volume of the hG air electrode expanded to form a thick layer outside the top SS wire mesh in the wave spring-induced space between the electrode and the perforated cathode cap. Therefore, the postmortem analysis of the cathode exhibited three distinct
discharge product layers (Figure 3a). The materials in each layer were thus facilely collected and analyzed.

**Figure 3.** (a) Schematics of the architecture of a fully discharged “analytical” hG air cathode with a SS wire mesh support, an Al mesh insertion to separate the middle and the bottom layers, and an Al mesh to allow facile separation of the electrode from the glass fiber membrane separator. (b) XRD and (c) FT-IR results of the three layers from a fully discharged hG air cathode with $m_A$ of 7 mg/cm$^2$ and a similar architecture to (a). SEM results of the top, middle, and bottom layers of the same electrode are shown in (d), (e), and (f), respectively.
Results from XRD patterns shown in Figure 3b suggested the discharge product contained mostly Li$_2$O$_2$ (ICDD# 09-0355), but both LiOH (ICDD# 85-1064) and Li$_2$CO$_3$ (ICDD# 22-1141) were also present. The corresponding FT-IR spectra shown in Figure 3c are consistent with the above findings, where the peaks for Li$_2$O$_2$ (~490 cm$^{-1}$), LiOH (~3700 cm$^{-1}$), and Li$_2$CO$_3$ (~1400 cm$^{-1}$) all appeared. In addition, lithium carboxylates (RCOOLi, R- = H- or CH$_3$-, ~1600 cm$^{-1}$) were also found. Both XRD and FT-IR data showed higher signal intensities of various discharge products in the top layer than those in the middle layer, while signal intensities from the bottom layer were comparably much weaker. Consistently, SEM results showed that the top layer contained a large amount of toroid-like discs that were of ~1 µm in diameter and ~400 nm in peripheral thickness (Figure 3d). Toroid-like discs are typical morphology for Li$_2$O$_2$ discharge products in Li-O$_2$ batteries.$^{1-3,49}$ The toroids were also populated in the middle layer with similar diameters but somewhat thinner in thicknesses (~300 nm) (Figure 3e). In the bottom layer, however, the hG sheets appeared to be mostly free from deposits, however some small toroids (400 – 800 nm in diameter, less than 200 nm in thickness) were occasionally found (Figure 3f).

The combination of battery performance and analytical data therefore conclusively supported the mechanism that the initial discharge products preferentially formed in the top layer that was in the closest proximity to O$_2$ atmosphere, and then gradually populated the middle layer. With the progress of discharge, the oxygen concentration in the bottom layer became critically low due to the blocking of the mass transport from the top and middle layer. When no more discharge products could be effectively formed, the cell failed.

The amount of cathode materials that were effectively utilized from the above layer-by-layer analyses (combined for ~4 mg/cm$^2$) was consistent with the results deducted from the battery performance with various air cathode mass loadings (Figure 2c). The “fully” discharged ultrathick hG electrodes ($m_A$ ~ 10 mg/cm$^2$ shown in Figure 2b & c) were likely not saturated with
discharge products, but exhibited a concentration gradient that gradually decreased from the air side through the electrode depth. The air side had the most product accumulation, while the separator/Li side was minimally utilized (Figure 2d). In thin electrodes with $m_A$ of 5 mg/cm$^2$ or less, all electrode materials were effectively used under the same current density (0.2 mA/cm$^2$).

For high capacity Li-O$_2$ batteries, the amount of Li anode used can become more relevant. The weight of Li chips used in this work was $\sim$40 mg, which corresponded to $\sim$90 mAh/cm$^2$, a safe excess in comparison to the highest areal capacity achieved by the ultrathick hG air cathodes ($\sim$40 mAh/cm$^2$). To confirm that the battery failure was indeed due to the blocking of air electrodes and not over-usage of Li, a fully discharged cell ($m_A \sim 10$ mg/cm$^2$, $I_m = 0.2$ mA/cm$^2$, $C_A \sim 40$ mAh/cm$^2$) was disassembled. The hG air electrode was removed and assembled into a new cell with a fresh Li chip. As shown in Figure S2 in Supporting Information, the reassembled cell exhibited a very small (< 3 mAh/cm$^2$) full discharge capacity before failure, confirming the above suggested hypothesis.

A possible solution to alleviate the blocking of oxygen diffusion channels is to prepare a more porous air electrode. To achieve this, an hG electrode was dry pressed at a lower pressure (60 MPa) under otherwise identical conditions. The stacking of hG sheets was less densified, as suggested by the reduced Barrett–Joyner–Halenda (BJH) pore volume (0.673 vs. 0.544 cm$^3$/g) measured by nitrogen adsorption-desorption experiments despite very similar Brunauer–Emmett–Teller (BET) surface area (309 vs. 304 m$^2$/g). Less densified hG sheet stacking could thus allow mass transport deeper into the electrode thickness for better electrode utilization. Indeed, at $m_A$ of 5.3 mg/cm$^2$, the air electrode prepared at 60 MPa exhibited a full areal capacity of $\sim$40 mAh/cm$^2$ (specific capacity $\sim$7450 mAh/g), $\sim$14% higher than the air electrode prepared at 200 MPa with similar $m_A$ (Figure S3 in Supporting Information). More in-depth studies are needed to correlate
the porosity and optimized electrode utilization. Most hG air electrodes in this work were still prepared with 200 MPa of compression pressure.

2.3. Discharge Products

A useful method to confirm the main discharge product was through the use of galvanostatic intermittent titration technique (GITT). In a typical GITT experiment, a cell that is being discharged is intermittently relaxed with no current flow for a prolonged period of time to allow the cell potential to gradually reach the equilibrium potential corresponding to the main discharge product. Li-O₂ cells with dry-pressed hG air cathodes with \( m_A \) of both 5 and 10 mg/cm² were subjected to GITT experiments, in which the cells were discharged for 5 h and relaxed for 5 h, and the process was repeated multiple times. As shown in Figure S4 in the Supporting Information, the relaxed cell potentials with hG air electrodes with \( m_A \) of both 5 and 10 mg/cm² were ~2.96 V, thus confirming that the main discharge product was indeed Li₂O₂.

A major side product found in discharged hG air cathodes was LiOH, which has been attributed to trace moisture present in the system (see Figure S5 and discussions in the Supporting Information). There were also small amounts of Li₂CO₃ and RCOOLi identified in the discharge product. A common source for these side products in Li-O₂ cells was from electrolyte decomposition. Minor oxidative corrosion of the high mass loading hG cathodes might have also occurred during ORR, but the majority of the cathode materials were stable.

2.4. Charge and Cycling Properties

Reversing the current flow after discharge resulted in the charging of the Li-O₂ cells, during which the discharge products decomposed to restore the battery, in an ideal case, to the original state via OER reactions. Our previous report showed that hG materials without doping
or additional metallic catalysts are reasonable (although improvable) OER catalysts in Li-O₂ batteries with low cathode mass loading \( m_A < 0.5 \text{ mg/cm}^2 \). With high mass loading dry pressed hG air cathodes \( m_A > 5 \text{ mg/cm}^2 \), the Li-O₂ cells became unstable when the charge Colomnic efficiency reached \( \sim 70\% \). To investigate a fully charged cell, the discharge capacity was thus limited to \( 20 \text{ mAh/cm}^2 \) (100 h at 0.2 mA/cm²), and the cell with \( m_A \) of 10 mg/cm² was able to charge at near 100% efficiency with a charge-discharge overpotential \( \Delta V_{C/2} \); measured at half discharge capacity) of \( \sim 1.2 \text{ V} \) (Figure 4a). The voltage instability at the end of charge was likely a combined effect from electrolyte exhaustion and deep stripping-plating of Li metal anode. FT-IR results (Figure 4b) showed that most discharge products (\( \text{Li}_2\text{O}_2 \), \( \text{LiOH} \), RCOOLi, and most \( \text{Li}_2\text{CO}_3 \)) were removed after charging. Low magnification SEM imaging (Figure 4c) confirmed the hG sheets in the charged electrode were free from large discharge products such as \( \text{Li}_2\text{O}_2 \) toroids. At higher magnification (Figure 4d), the individual hG sheet surfaces appeared clean and largely free from deposits, very similar to the morphology of pristine hG sheets (Figure 1a). The surface holes of hG sheets were readily visible; no obvious diameter enlargement was found. These results strongly suggested that the dry pressed hG air electrodes are stable and an excellent platform for rechargeable Li-O₂ cells.
Figure 4. (a) Voltage profiles and (b) the corresponding FT-IR spectra of (i) a fully discharged cell and (ii) a fully charged cell after a 100 h discharge-100 h charge cycle both with hG air electrodes with $m_A$ of 10 mg/cm$^2$ at 0.2 mA/cm$^2$. (c) and (d) are SEM images at different magnifications of the above charged hG air electrode.

The cycling performance of Li-O$_2$ cells with dry-pressed hG air cathodes was further investigated at curtailing capacities, with discharge and charge potential limits set at 2.0 and 4.5 V, respectively. As shown in Figure 5a and b, when the curtailing areal capacity was set at 2 mAh/cm$^2$ (projected lower limit of practical EV batteries)$^{1-3}$ at 0.2 mA/cm$^2$, the cycling of a Li-O$_2$ cell with a hG air cathodes with $m_A$ of 5 mg/cm$^2$ could persist 15 cycles with no reduction in the curtailing discharge capacity. However, the charging started to reach the upper voltage limit as early as the 7th cycle, with the efficiency deteriorating after 13 cycles. In comparison, the cyclability of a hG air cathode with $m_A$ of 10 mg/cm$^2$ was much enhanced under the same experimental conditions. As shown in Figure 5c and d, the voltage profiles of the higher mass
loading electrode was relatively stable for nearly 20 cycles. At cycle 20, the discharge and charge areal capacities for the air cathode with \( m_A \) of 5 mg/cm\(^2\) significantly dropped to 1.2 and 0.8 mAh/cm\(^2\), respectively, while both of those maintained at 1.7 mAh/cm\(^2\) when using the higher mass loading electrode (\( m_A \) of 10 mg/cm\(^2\)). The overpotential comparison of the two cells exhibited a similar trend (Figure S6 in the Supporting Information). The overpotential values (measured at 1 mAh/cm\(^2\)) for the 10 mg/cm\(^2\) electrode were slightly smaller than those for the 5 mg/cm\(^2\) one for the first 10 cycles (1.45-1.55 vs. 1.50-1.65 V). The former remained relatively stable for 20 cycles, while the latter significantly deteriorated after 13 cycles. In the literature, there were reports on high cycle numbers (50 or more) for Li-O\(_2\) batteries with undoped graphene-based air cathodes, but they were usually obtained with a low curtailing capacity of 0.25 mAh/cm\(^2\) or less at an areal mass loading not exceeding 0.5 mg/cm\(^2\) (Table S3 in the Supporting Information).
Figure 5. (a,c) Voltage profiles and (b,d) the corresponding cycling dependence of discharge (D) and charge (C) areal capacities and Colomnic efficiency of Li-O2 cells with dry pressed hG air electrodes. The $m_A$ values were (a,b) 5 and (c,d) 10 mg/cm², respectively. The current density was 0.2 mA/cm² and the curtailing capacity was 2 mAh/cm².

Several factors might have contributed to the enhanced cyclability of the cells with higher mass loading cathodes. First, at the same areal current density $I_A$, the higher mass loading cathodes experienced lower gravimetric current density $I_m$, which is more favorable for stable discharge and charge events. Second, with total areal capacity kept the same (2 mAh/cm²), the same amount of discharge products were distributed in a larger architecture in the higher mass loading cathodes (despite the preferential location near the air side; see below). Repeated filling/emptying the pores during cycling thus had less of a mechanical effect on the electrode structure.
In order to investigate the cell failure mechanism, similar cycling experiments were stopped at different reaction stages, and the postmortem analyses of the air cathodes were conducted. Because the total capacity of the thick (~5 mg/cm²) and ultrathick (~10 mg/cm²) electrodes could be as high as ~40 mAh/cm², the above depth of cycling was only ~5% of the total capacity. By analyzing the top (air side) and bottom (separator/lithium side) of the electrodes at the end of discharge during cycling (Figure S7 in the Supporting Information), it was confirmed that most discharge products formed on the air side of the air electrode facing the perforated opening of the cathode cap. For convenience of discussion, all data shown are results from specimens carefully isolated from the top layer of the electrodes. FT-IR and SEM were chosen as the representative spectroscopic and microscopic tools, respectively, for the product characterization.

With a shallow discharge, the amount of the battery reaction products formed were much less than those from deep discharge shown previously in Figure 3. For example, an hG air electrode with $m_A \sim 5$ mg/cm² after the first discharge of 2 mAh/cm² at 0.2 mA/cm² exhibited weak FT-IR signals of Li$_2$O$_2$ and LiOH with very small amount of Li$_2$CO$_3$ (Figure 6a). Consistently, the SEM image of the electrode material showed Li$_2$O$_2$ toroids of ~1 μm in diameter and ~200 nm in thickness decorating the surfaces of the hG sheets (Figure 6b). After the subsequent 10 h charge to complete the first cycle, all FT-IR product peaks became much weaker (Figure 6a), and the hG sheet surface appeared free from coating of discharge products (Figure 6c). While both Li$_2$O$_2$ and LiOH were still observed in the FT-IR spectra of the discharge products from the 3rd and 9th cycle, a significant difference is that the signals from Li$_2$CO$_3$ and RCOOLi became much stronger. The shapes of the discharge products were less defined with the presence of some amorphous coating (Figure 6d). FT-IR of the charged products from later cycles (e.g., 10th charge) showed the presence of Li$_2$CO$_3$ and RCOOLi.
byproducts, indicating incomplete removal of some of the discharge products (Figure 6a). Consistently, the hG sheet surfaces exhibited an amorphous coating most likely from the byproduct residue (Figure 6e). The hG sheet integrity during cycling experiments was investigated using Raman spectroscopy. As shown in Figure S8 in the Supporting Information, the D/G ratios and the peak widths for the cathode materials at different stages of cycling were very similar, suggesting that there was no significant degradation of hG sheets in the air electrodes under current cycling conditions.

![Figure 6](image.png)

**Figure 6.** Characterization of dry-pressed hG air electrodes after cycling ($m_A \sim 5$ mg/cm$^2$; $I_A = 0.2$ mA/cm$^2$): (a) FT-IR spectra for products (from bottom to top) after 1$^{\text{st}}$ discharge, 1$^{\text{st}}$ charge, 3$^{\text{rd}}$ discharge, 3$^{\text{rd}}$ charge, 9$^{\text{th}}$ discharge, and 10$^{\text{th}}$ charge. SEM images were shown for products after (b) 1$^{\text{st}}$ discharge, (c) 1$^{\text{st}}$ charge, (d) 9$^{\text{th}}$ discharge and (e) 10$^{\text{th}}$ discharge.

The above results strongly suggested that the cell failure after multiple charge/discharge cycles was arising from the deactivation of the catalytic centers on the hG sheet surfaces at the air side by the accumulation of less reversible discharge products such as Li$_2$CO$_3$.$^{52,53}$
deactivated hG sheets on the top electrode surface, although only consisting of a small amount of total electrode material, likely prevented the mass transport into deeper electrode architecture after a number of cycles. It is therefore imperative to incorporate more active OER catalysts to reduce the charge overpotential and alleviate such blocking, thereby further improving the cycling performance of these ultrathick hG air cathode platforms.

3. Conclusions

The unique dry compressibility of hG enabled the facile preparation of high mass loading electrodes under solvent-free and binder-free conditions. These electrodes were directly used as air cathodes for Li-O₂ batteries that exhibited unprecedented ultrahigh areal capacity values (as high as ~40 mAh/cm²) ever reported for carbon-only electrodes under deep discharge conditions. The battery reactions were reversible, rendering excellent cyclability even at a high curtailing capacity (2 mAh/cm²). Characterizations of postmortem electrodes showed that the discharge products preferentially accumulated first on the air side and exhibited a gradient into the thick electrode architecture. Under deep discharge conditions, the total areal capacity saturated at a medium mass loading (~5 mg/cm² under current experimental conditions) when the discharge product accumulation at the air side blocked the further oxygen entry. The failure mode for battery cycling was more likely due to the deactivation of catalytic centers from the accumulated coating of less reversible discharge products such as Li₂CO₃ over multiple cycles. Ultrathick electrodes (e.g., mass loadings of 10 mg/cm²) were found advantageous in improved cyclability, most likely because of the reduced gravimetric current density and better mechanical support during cycling.

This work was only focused on the hG air cathode platform itself. It is highly anticipated that further optimization of cathode material (e.g. heteroatomic doping onto hG structure and
catalytic decoration onto hG surface), cathode architecture (e.g. precise catalyst placement), and
electrolyte (e.g. the use of a redox mediator in combination with a stable electrolyte) will further
improve the Li-O\textsubscript{2} battery performance. Research in these various directions are currently
underway in our laboratories.

4. Methods

\textit{hG Synthesis.} In a typical experiment, the starting graphene powder (~1.5 g; Vorbeck
Materials; Vor-X; grade: reduced 070; lot: BK-77x) was placed in a quartz boat and heated to
430 °C in static air with an open-ended tube furnace (MTI Corporation OTF-1200X-80-II) at a
ramp rate of 10 °C/min and held isothermally for 10 h. The final hG product (~70% yield) was
directly collected after cooling down the reaction.

\textit{hG Air Electrode Preparation.} hG air electrodes were all prepared using a facile solvent-
free compression approach. In a typical experiment, a piece of precisely cut (15 mm in diameter)
separation layer (i.e., a piece of SS woven wire mesh, Al perforated mesh, or Celgard membrane;
all obtained from MTI Corporation) was first loaded in a stainless steel pressing die with an inner
diameter of 14.85 mm (MTI Corporation; Model EQ-Die-15D), followed by a measured amount
of hG powder (~3 – 20 mg in this work), and then another piece of separation layer. The die was
then placed in a hydraulic press (Carver Hydraulic Unit Model #3925) and a load of ~8000 lbs
(equivalent to ~200 MPa) was applied. After 15 minutes, the die was unloaded, and the pellet
was removed from the die. Electrodes prepared with Celgard membrane separation layers were
made freestanding by gently peeling off both plastic discs. Those with SS woven wire meshes or
Al perforated meshes were used as fabricated.

\textit{Multilayer “Analytical” Air Cathodes.} To enable facile isolation of electrode materials at
different depths with minimal added physical and electrical impedance, one or more extra
perforated Al mesh insertions were used. In a typical preparation procedure to prepare an analytical air cathode with one Al mesh (bottom piece; for facile separation of the wet electrode material from the glass fiber membrane separator), half of the hG electrode material, another Al mesh (insertion), the other half of the hG electrode material, and finally a SS wire mesh (top current collector and structural support) were sequentially loaded into the same pressing die (MTI Corporation; Model EQ-Die-15D) and subjected to hydraulic compression under the same conditions as the regular air cathodes. The resultant disc was one robust piece that was directly used as the cathode in a Li-O₂ battery following the typical assembling procedure (see below).

**Li-O₂ Battery Assembly.** The Li-O₂ batteries were assembled in the format of CR2032 coin cells in an Ar-filled glove box. 1 M lithium bis(trifluoromethane)sulfonimide (LiTFSI; Sigma-Aldrich, 99.95%) in tetraethylene glycol dimethyl ether (TEGDME; Sigma-Aldrich, ≥99%) was used as the electrolyte. A “bottom-to-top” assembly process was used to avoid losing cathode materials through the perforated cathode cap. In such a process, a piece of precisely cut copper foil (15 mm in diameter; as the anode current collector) and a Li chip (15.6 mm in diameter; 0.45 mm in thickness; as the anode; MTI Corporation, EQ-Lib-LiC45) were placed in a SS anode cap with a built-in isolation ring (MTI Corporation), followed by addition of 90 µL of the electrolyte. A piece of glass fiber membrane (19 mm in diameter; as the separator) was then placed on top of the wet Li chip to cover the entire anode cap opening. Another 90 µL of electrolyte was added to wet the membrane. The hG air electrode was then centered on top of the membrane, followed by the addition of 90 – 120 µL of electrolyte to completely wet the electrode. After placing a SS wave spring (MTI Corporation) on top of the wet air electrode, a perforated cathode cap (MTI Corporation) was carefully placed on the very top and gently pushed down to encase the anode cap. The entire assembly was placed in a hydraulic crimping device (MTI Model MSK-110) and crimped at a pressure of ~800 psi into a functional coin cell battery.
**Li-O₂ Battery Testing.** The Li-O₂ coin cells were tested in a custom made air-tight box with continuous flow (30 – 100 mL/min) of pure oxygen using either a multi-channel battery analyzer (MTI Corporation; Model BST8-MA) or a multi-channel electrochemical station (Bio-Logic; Model VMP3). The discharge and charge voltage limits were set at 2.0 and 4.5 V, respectively. Areal current densities of 0.1, 0.2, and 0.5 mA/cm² were used for the deep discharge experiments, while 0.2 mA/cm² was used for the cycling experiments with 10 h each for discharge and charge events, respectively. The areal current density values were calculated based on the area of the air electrode (1.73 cm²). Therefore, the actual current used for 0.1, 0.2, and 0.5 mA/cm² were 0.173, 0.346, and 0.865 mA, respectively.⁵⁴

**Other Measurements.** Scanning electron microscopy (SEM) images were acquired using a Hitachi S-5200 field emission SEM (FE-SEM) system at an acceleration voltage of 30 kV. A Rigaku SmartLab X-ray Diffractometer with a Cu Kα radiation source was employed for X-ray diffraction (XRD) analyses. FT-IR measurements were conducted on a Thermo Scientific Nicolet iS5 FT-IR spectrometer equipped with an iD7 ATR diamond optic accessory. Raman spectra were acquired with an excitation wavelength of 532 nm on a Thermo-Nicolet-Almega Dispersive Raman Spectrometer. Nitrogen adsorption-desorption isotherms and the corresponding BET surface area values and BJH pore characteristics were acquired on a Quantachrome Nova 2200e Surface Area and Pore Size Analyzer system using a 9-mm bulbless cell.

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Supporting Information Available. This material is free of charge from the journal website or from the authors.

References


Ultrahigh Capacity Lithium-Oxygen Batteries Enabled by Dry-Pressed Holey Graphene Air Cathodes

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Figure S1. (a,b) Typical SEM images of dry-pressed hG air cathodes with perforated Al mesh supports. (c) Full discharge voltage profile comparison for Li-O$_2$ batteries with dry-pressed hG air cathodes with SS woven mesh support, with Al mesh support, and with no support and thus freestanding. The mass loadings were all ~10 mg/cm$^2$; $I_A = 0.2$ mA/cm$^2$.
Figure S2. Full discharge profile (black) of a typical Li-O$_2$ cell with a dry-pressed hG air cathode with $m_A \sim 5$ mg/cm$^2$ at $I_A = 0.2$ mA/cm$^2$. The cell was then disassembled, and the discharged air electrode was incorporated into a new cell with a fresh Li chip, a new glass fiber membrane separator and electrolyte. The voltage profile for the reassembled cell at the same current density is shown in red.
Figure S3. Full discharge profiles at \( I_A = 0.2 \, \text{mA/cm}^2 \) of two Li-O\(_2\) cells with dry-pressed hG air cathodes (\( m_A \approx 10 \, \text{mg/cm}^2 \) for both) prepared under compression pressures of 200 (black, solid) and 60 MPa (green, dashed), respectively.
Figure S4. GITT experiments (5 h discharge, 5 h relax) of two Li-O₂ cells with dry-pressed hG electrode mass loading of (a) 5 mg/cm² and (b) 10 mg/cm², respectively, at $I_A = 0.2$ mA/cm².
Figure S5. XRD patterns of Li-O₂ cells with (top) a carefully dried dry-pressed hG air cathode in a well-sealed oxygen chamber and (bottom) a dry-pressed hG air cathode in an oxygen chamber with moisture contamination. The mass loading in both cases were 5 mg/cm²; the current density was 0.2 mA/cm². Although no intensive drying procedure was applied to the electrolyte solution used in this work, fresh lithium chips immersed in the electrolyte but stored in an Ar-filled glovebox retained their shiny surface for over three months, indicating that no moisture is present. Thus, the moisture that resulted in LiOH formation was unlikely from the electrolyte. The data shown in Figure S5 above therefore suggested the moisture contamination in the oxygen chamber was the main cause for the LiOH formation.
Figure S6. Overpotential comparison for cycled Li-O\(_2\) cells with mass loadings of 5 and 10 mg/cm\(^2\). The discharge and charge voltages were both measured at 1 mAh/cm\(^2\).
Figure S7. FT-IR spectra of the top (red) and bottom (blue) sides of a dry-pressed hG air electrodes after 3\textsuperscript{rd} discharge \((m_A \sim 5 \text{ mg/cm}^2; I_A = 0.2 \text{ mA/cm}^2)\), showing that the majority of the discharge products formed on the top.
**Figure S8.** Raman spectra for a hG air cathode after various discharge and charge cycles: (from bottom to top) 1st Discharge, 1st Charge, 3rd Discharge, 3rd Charge, 9th Discharge, and 10th Charge.
Table S1. Full discharge characteristics of Li-O₂ cells with dry-pressed hG cathodes of various mass loadings.

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<th>Mass Loading (mg/cm²)</th>
<th>Specific Capacity (mAh/g)</th>
<th>Areal Capacity (mAh/cm²)</th>
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Table S2. Full discharge properties of previously reported Li-O_2 batteries with graphene-based (no doping or additional catalyst) air cathodes in comparison to this work. Underlined numbers were calculated or estimated based on available data in the respective reports.

<table>
<thead>
<tr>
<th>Material</th>
<th>Electrode Preparation</th>
<th>Mass Loading (mg/cm^2)</th>
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<th>Capacity</th>
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¹³: ref. ¹³, ¹⁴: ref. ¹⁴, ¹⁵: ref. ¹⁵, ¹⁶: ref. ¹⁶, ¹⁷: ref. ¹⁷, ¹⁸: ref. ¹⁸, ¹⁹: ref. ¹⁹, ²⁰: ref. ²⁰, ²¹: ref. ²¹, ²²: ref. ²², ²³: ref. ²³.
**Table S3.** Cycling properties of previously reported Li-O\textsubscript{2} batteries with graphene-based air cathodes (no doping or additional catalyst) in comparison to this work. Underlined numbers were calculated based on available data in the respective reports.

<table>
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<td>0.8 mg (total weight)</td>
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<td>Slurry</td>
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<td>Graphene with Mesoporous Carbon</td>
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<td>1M LiTFSI in TEGDME</td>
<td>100</td>
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<td>Vacuum-promoted, thermal-expanded graphene</td>
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<td>0.1M LiClO\textsubscript{4} in DMSO</td>
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<td>rGO</td>
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<td>0.3-0.5 mg (total weight)</td>
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<td>200</td>
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<td>600</td>
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<tr>
<td>rGO</td>
<td>Slurry</td>
<td>0.1</td>
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Table S3 (continued)

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<th>Material</th>
<th>Electrode Preparation</th>
<th>Mass Loading (mg/cm²)</th>
<th>Electrolyte</th>
<th>Current Density (mA/g)</th>
<th>Curtailing Capacity (mAh/g)</th>
<th>Number of Cycles</th>
<th>Publication Year</th>
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<td>Mass Loading (mg/cm²)</td>
<td>Electrolyte</td>
<td>Gravimetric (mA/g)</td>
<td>Areal (mA/cm²)</td>
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<td>1 M LiCF₃SO₃ in TEGDME</td>
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<td>GNP/GO Paper</td>
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<td>0.8 mg</td>
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<td>100</td>
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<td>500</td>
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<tr>
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Binder-Free Electrodes
References:


