ACCOUNTS of chemical research

pubs.acs.org/accounts Article

Scalable Dry-Pressed Electrodes Based on Holey Graphene

Yi Lin,* Christian O. Plaza-Rivera, Liangbing Hu,* and John W. Connell[||]

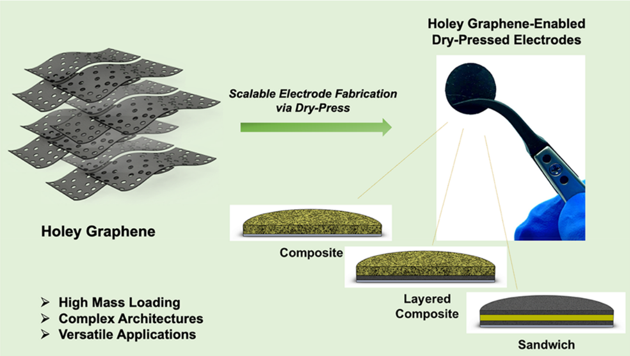
Cite This: *Acc. Chem. Res.* 2022, 55, 3020−3031 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

CONSPECTUS: Holey graphene (hG) is a structural derivative of graphene with arrays of through-thickness holes of a few to tens of nanometers in diameter, randomly distributed across the nanosheet surfaces. In most bulk preparation methods, the holes on hG sheets are preferentially generated from the pre-existing defects on graphene. Therefore, contrary to intuitive belief, hG is not necessarily more defective than the intact graphene. Instead, it retains essential parent properties, including high electrical conductivity, high surface area, mechanical robustness, and chemical inertness. Furthermore, the added holey structural motif imparts unique properties that are not present in unmodified graphene, making hG advantageous in numerous applications such as sensing, membranes, reinforcements, and electrochemical energy storage. In particular, the presence of holes enhances the mass transport through the nanosheet plane and thus significantly reduces tortuosity. This difference is a key advantage for using hG in energy storage applications where the transport of ions through the thickness becomes more hindered as the electrode thickness increases to meet practical energy density requirements.

An unexpected discovery is that the holes of the hG sheets enable the dry hG powder to be directly compressed into robust monoliths. hG not only can be pressed into monoliths by itself but also can host other electrochemically active materials as a compressible matrix. This important yet unique property, which is not available for other carbon materials including intact graphene, significantly broadens the application horizon in energy storage applications. With the dry compressibility, electrodes with ultrahigh mass loading and thus ultrahigh areal capacity may be conveniently fabricated without toxic solvents or parasitic binders, which are required in conventional slurry-based approaches for electrode fabrication. The dry-press electrode preparation process can be completed within minutes regardless of mass loading. In comparison, high-mass-loading electrodes for advanced battery chemistries using conventional fabrication methods often need stringent and time-consuming process control. hG can also be combined with electrochemically active battery materials while maintaining dry compressibility. This has allowed the unprecedented, convenient manipulation of a wide variety of thick electrode compositions and architectures, which provides not only outstanding performance but also new physical insights for various battery chemistries.

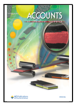
In this Account, we first present some basic observations on the dry compressibility of hG as well as the mechanistic investigations from atomistic modeling rationalizing this unique property. We then showcase the applications of neat and composite dry-pressed hG electrodes for various energy storage platforms including supercapacitors, lithium (Li) ion batteries, Li−O_2 batteries, and Li−S/Se batteries. The preparation and performance of thick electrodes with practical mass loadings and unique electrode architecture manipulation, both enabled by the dry compressibility of hG, are highlighted and discussed.



KEY REFERENCES

- Han, X.; Yang, Z.; Zhao, B.; Zhu, S.; Zhou, L.; Dai, J.; Kim, J.-W.; Liu, B.; Connell, J. W.; Li, T.; Yang, B.; Lin, Y.; Hu, L. Compressible, Dense, Three-Dimensional Holey Graphene Monolithic Architecture. *ACS Nano* **2017**, *11*, 3189−3197.[26]
- Lin, Y.; Moitoso, B.; Martinez-Martinez, C.; Walsh, E. D.; Lacey, S. D.; Kim, J.-W.; Dai, L.; Hu, L.; Connell, J. W. Ultrahigh-Capacity Lithium-Oxygen Batteries Enabled by Dry-Pressed Holey Graphene Air Cathodes. *Nano Lett.* **2017**, *17*, 3252−3260.[34]
- Kirsch, D. J.; Lacey, S. D.; Kuang, Y.; Pastel, G.; Xie, H.; Connell, J. W.; Lin, Y.; Hu, L. Scalable Dry Processing of Binder-free Lithium-ion Battery Electrodes Enabled by Holey Graphene. *ACS Appl. Energy Mater.* **2019**, *2*, 2990−2997.[29]
- Plaza-Rivera, C. O.; Walker, B. A.; Tran, N. X.; Viggiano, R. P.; Dornbusch, D. A.; Wu, J. J.; Connell, J. W.; Lin, Y. Dry Pressing Neat Active Materials into Ultrahigh Mass Loading Sandwich Cathodes Enabled by Holey Graphene Scaffold. *ACS Appl. Energy Mater.* **2020**, *3*, 6374−6382.[32]

Received: July 6, 2022
Published: September 29, 2022



ACS Publications

https://doi.org/10.1021/acs.accounts.2c00457

1. INTRODUCTION

Carbon nanomaterials, including fullerenes, carbon nanoparticles, carbon nanotubes, and graphene, are a remarkable family of materials that has inspired more than three decades of nanoscience and nanotechnology research and development for a broad array of applications.[1] Graphene, the two-dimensional (2D) member of this family, exhibits chemical stability, high mechanical strength, a large surface area, and outstanding electrical and thermal conductivity yet has a thickness of just one atomic layer (or a few layers for few-layered graphene).[2] The combination of its properties and 2D structure has made it one of the most popular materials used in applications such as electronics, sensing, coatings, reinforcements, and energy conversion and storage.[3]

Mechanical exfoliation and chemical vapor deposition methods provide high-quality graphene sheets with controlled thicknesses and large lateral sizes. However, for applications that require a bulk quantity of materials such as composite fillers and battery electrodes, graphene is often prepared via the oxidative exfoliation of natural graphite to form graphene oxide (GO) followed by chemical or thermal reduction.[4] These GO-derived graphene materials are usually rich in surface defects, which is not necessarily a shortcoming because it can provide opportunities for further chemical modifications. The functionalization of graphene sheets typically refers to the attachment of organic moieties (such as functional groups, molecules, or polymer chains)[5] and inorganic particles (such as metal or metal oxide nanoparticles)[6] or heteroatomic doping (i.e., the replacement of surface carbon atoms with heteroatoms such as nitrogen, boron, and sulfur).[7] These graphene derivatives can provide improved performance in the various applications mentioned above.

Holey graphene (hG) is also a structural derivative of graphene.[8] For hG, instead of additional atoms or moieties, groups of carbon atoms are removed from the sheet surface, resulting in an array of holes while still retaining the 2D structure. At first sight, it appears that graphene sheets become more "defective" with the holes. This is not necessarily the case because the holes largely originate from the intrinsic defect sites of the starting graphene material. Therefore, as long as the hole generation method is sufficiently mild, the remaining carbon network maintains its graphitic properties, which is reflected in minimal changes in electrical and mechanical properties as observed experimentally.[9] Various methods such as liquid-phase oxidation and air oxidation used to convert graphene into hG have been reported, as summarized in several recent reviews.[8,10,11] Controlled air oxidation, with metal catalysts or catalyst-free, has been used in our laboratory to produce hG in scalable processes.[12−14] (See the extended discussions in the Supporting Information.)

The presence of nanometer-sized holes through the vast lateral area of the 2D graphene sheets brings about new functions. Among the most explored is the much enhanced through-thickness mass transport and, as a result, the more accessible graphitic surface area in the stacks of nanosheets.[13,15−17] Although the transport of ions and molecules through stacks of intact graphene sheets needs to go around the large lateral surfaces, the presence of holes significantly reduces this tortuous pathway (Figure 1). This feature is especially important for energy storage applications, where hG is used as an electrode material and the holes are the facile passages for electrolyte molecules and various ions. We note that the holes on hG sheets should be conceptually differentiated from conventionally defined pores in assemblies of carbon nanomaterials and porous graphene.[8] The holes are intrinsic to the 2D hG nanosheet structure, and the pores refer to the voids and spaces between adjacent graphitic surfaces.

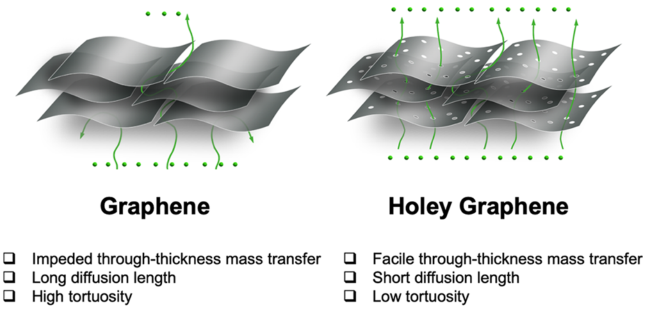


Figure 1. Schematic illustration: holey graphene, a structural derivative of graphene, exhibits enhanced through-plane mass transport and thus reduced tortuosity across the stacked nanosheets. The green dots refer to transporting masses such as ions or molecules. Reproduced with permission from ref 13. Copyright 2014 American Chemical Society.

Graphene has been considered to be one of the most attractive conductive constituents in electrodes for various energy storage systems.[18,19] As a structural derivative of graphene with improved properties, hG has naturally become an advanced alternative to intact graphene in all of these applications. Our group has shown that hG and its functionalized versions are outstanding electrode materials that are advantageous over intact graphene in different applications.[13,20−25] Demonstrated examples include supercapacitors, lithium (Li) ion battery anodes, and Li−O_2 and Li−CO_2 battery cathodes. (See the extended discussions in the Supporting Information.) Reviews in other applications of hG are also available in the literature.[8,10,11]

In this Account, we will focus on the dry compressibility of hG powder, which is not available to any other carbon allotropes to the best of our knowledge.[26] This unique feature enables facile, solvent-free, and binder-free electrode fabrication, bringing forward broad applications in a variety of energy storage systems. It is demonstrated that hG can be used directly for neat electrodes or as a matrix material for composite electrodes, all of which are prepared via dry powder compression at room temperature. The function of hG in these electrode systems has surpassed their conventional role as merely conductive additives because it functions as both a conductive scaffold and a binder. This provides a tremendous advantage in the facile and scalable fabrication of ultrahigh mass loading battery electrodes for practical applications.

2. DRY COMPRESSIBILITY OF HOLEY GRAPHENE

An outstanding and unique property of hG powder is its dry compressibility, an unexpected but logical consequence of the combination of the 2D nanostructure and the presence of holes throughout each nanosheet. More specifically, the as-produced hG powder was found to be compressible and moldable at room temperature into a variety of robust condensed shapes under completely solvent-free and binder-free conditions (Figure 2a).[26] This characteristics is absent in all other neat carbon materials (e.g., graphene, carbon nanotubes, graphite, and activated carbon) to the best of our knowledge. Although some materials such as graphite and carbon black may be compressed, the resultant architectures were extremely fragile and impossible

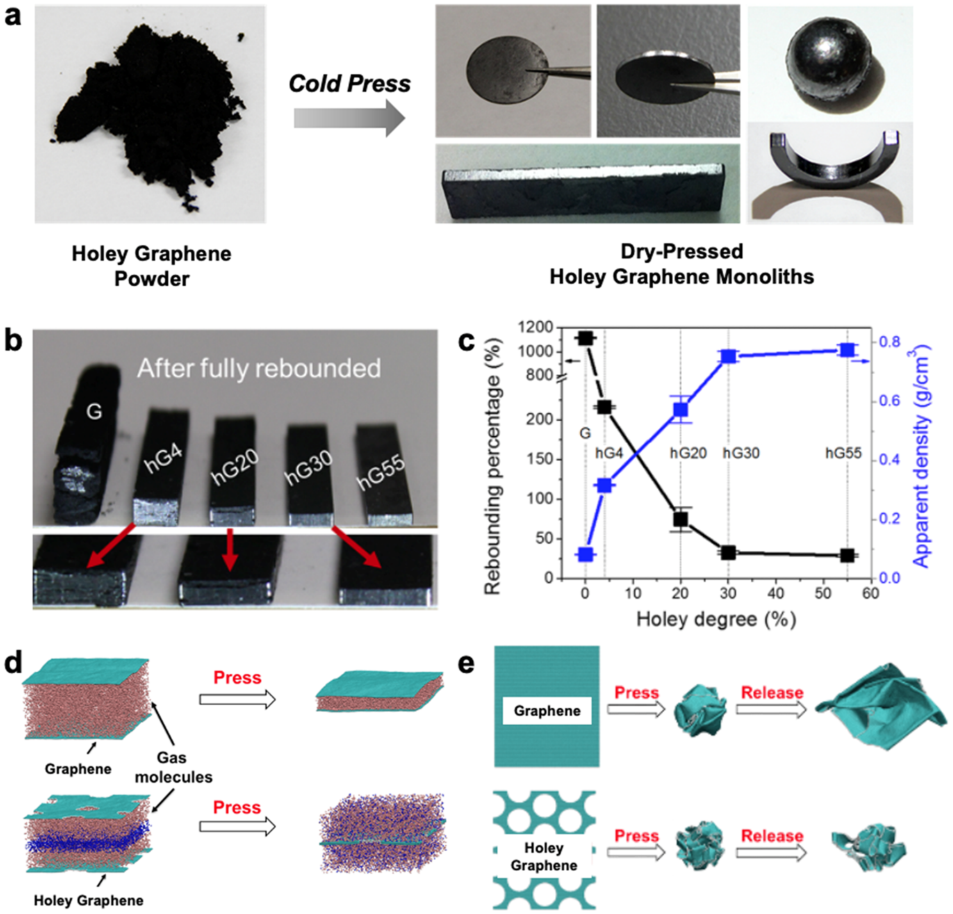


Figure 2. (a) Photographs of hG powder and its monoliths with various geometries fabricated by a cold press in a binder-free dry process. The dimensions of the monoliths shown are all in the range of 1−6 cm. (b) Photograph showing the increased density of various monolithic bars of hG at the increased holey degree (i.e., the percentage weight loss after air oxidation, indicated by the number). (c) Relationships between the rebounding percentage and the apparent density of the same monolithic bars based on the holey degree. (d, e) Atomistic simulations revealing the mechanism of the dry compressibility of hG. Reproduced with permission from ref 26. Copyright 2017 American Chemical Society.

to handle. Monolithic hG architectures obtained from such dry compression are robust and can survive repeated drop tests. The specific strength of the monoliths was as high as ∼18 MPa/(g/cm^3), in comparison to ∼8−13 MPa/(g/cm^3) for conventional graphite. The compressibility of hG was found to be related to the extent of hole formation (or "holey degree"), with hG of a higher holey degree exhibiting higher densification properties upon compression (Figure 2b,c). The compressed hG monoliths had densities of as high as 1.4 g/cm^3, but remained highly porous with surface area values in the range of 300−400 m^2/g.

Atomistic simulations suggested two key attributes that lead to the dry compressibility of hG (Figure 2d,e).[26] First, the presence of holes enables air to readily escape from the compressed architecture so that the nanosheets can be stacked in a densified fashion without trapped gas molecules. Second, the hole-edge functional groups allow improved adhesion between the adjacent nanosheets in the stack, in comparison to the lack of such in the parent intact graphene sheets. These two attributes collectively enable the hG sheets to be compressed under an applied force and stay densified with negligible rebounding upon removal of said force. In comparison, the removal of the compression force from compacted intact graphene sheets resulted in significant volume rebounding and thus weak architectures (Figure 2b). Importantly, neither solvent nor binder is needed to keep hG monoliths intact, making the process rapid, environmentally friendly, low cost, and extremely facile.

3. DRY-PRESS ELECTRODE FABRICATION ENABLED BY HOLEY GRAPHENE

Slurry-based electrode fabrication is the most common method that is widely used in industry and academic research laboratories.[27] In this approach (Figure 3a), the active battery material is dispersed in a solvent to form a concentrated dispersion (i.e., "slurry"), followed by casting the slurry onto a current collector foil. A polymer binder and conductive carbon are added to achieve desirable mechanical integrity and electrical conductivity of the formed electrode, respectively. To better disperse the electrode composite, a high-boiling-point organic solvent, such as NMP (*N*-methyl-2-pyrrolidone), is usually required. The subsequent removal after casting may thus cause environmental concerns. Water-based fabrication processes have also been developed for certain types of electrodes along with aqueous friendly polymer binders. Nonetheless, the slurry-based process remains time-consuming, with concerns of the polymer binder undergoing parasitic side reactions during battery cycling. Regardless of the solvent/liquid used, slurry-based methods make the fabrication of thick electrodes challenging.

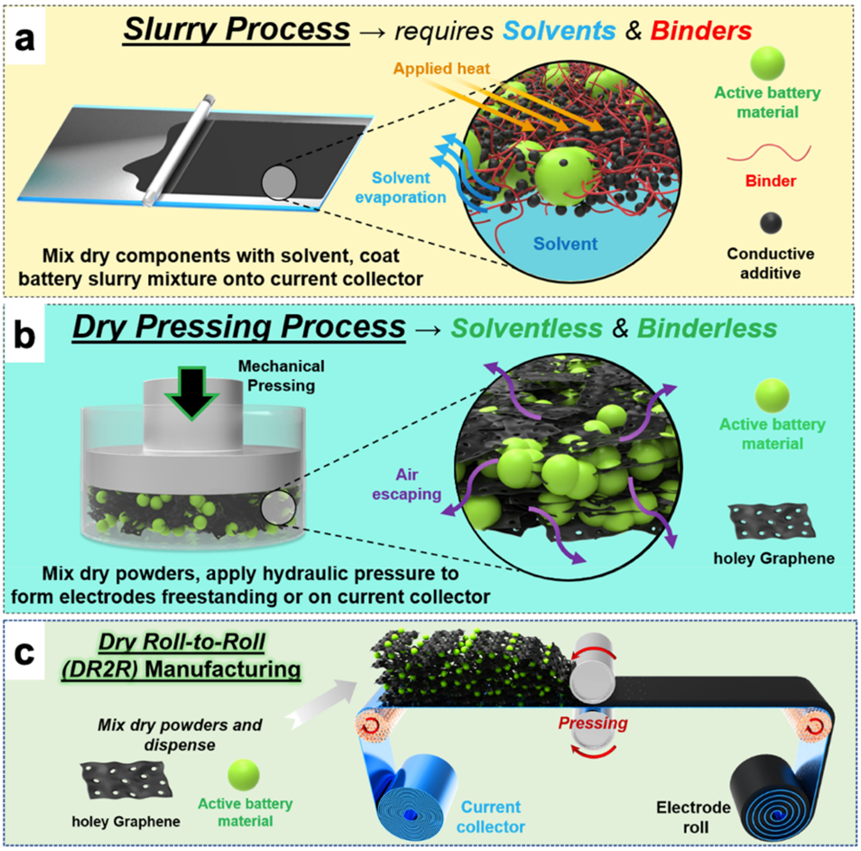


Figure 3. Comparison of (a) the conventional slurry process and (b) the holey-graphene-enabled dry pressing process in electrode fabrication. In the slurry process, binders, conductive additives, hazardous solvents, and post-fabrication energy and time inputs are required to create a uniform cast film. In the dry-pressing process, hG is added as a dry-pressable matrix to host battery active materials to create binderless, solventless electrodes at room temperature using only hydraulic pressure. (c) Future perspective of the proposed dry-press method to fabricate composite electrodes in a manner similar to conventional R2R battery electrode manufacturing. Reproduced with permission from ref 29. Copyright 2019 American Chemical Society.

The discovery of the dry compressibility of hG brings about a new application narrative for more efficient battery electrode manufacturing in terms of facileness, cost reduction, and environmental friendliness. In addition to the enhanced through-plane ion transport as an advanced replacement for graphene and other conductive carbon, hG can now conveniently serve as a unique conductive scaffold. The use of hG enables electrode fabrication through dry pressing, which is a facile, solvent-free, and room-temperature method that is universally applicable to various energy storage systems including, but not limited to, supercapacitors,[28] Li ion batteries,[29,30] Li−S/Se batteries,[31−33] and Li−O_2/air batteries.[34−37] As a conductive scaffold, hG not only can be pressed by itself into neat carbon electrodes but also can serve as a compressible matrix for hosting active battery materials or catalysts that otherwise cannot be dry pressed into robust architectures themselves. For the latter, because of the highly exfoliated nature of hG powder before compression (apparent density <10 mg cm^{-3}), the active battery materials or the functional electrocatalysts may consist of a high fraction (e.g., 90 wt %) of the total weight, but the composite power mixture retains a large volume and thus remains compressible. The highly exfoliated hG sheets also enable easy penetration of the dense filler powders to form homogeneous mixtures via a short, moderate mixing process.

In a typical procedure to prepare an electrode disc via dry pressing (Figure 3b), a desirable amount of hG powder or an hG-containing composite powder mixture is loaded into a pressing die and directly pressed into a desirable shape, such as round discs for coin cells or rectangles for pouch cells. The entire process from starting powder to a final electrode takes only minutes to complete, compared to the very lengthy procedure needed for the slurry-based approach and other solvent-based processes. In addition, the dry-press procedure is especially favorable for high material mass loading by simply adding more powder to the pressing die. The entire process is still completed within the same amount of fabrication time. In practical battery systems, high active material mass loading is critical to increasing the weight percentage of the active material in the final battery package, thus improving the overall energy density at the battery pack level. Achieving high mass loading has been a challenge in the slurry-based process, where repeated drying−casting cycles are usually required. For certain active materials for advanced battery chemistries such as S, electrode cracking beyond a certain mass loading threshold (~ 5 mg cm^{-2}) was often observed from slurry casting. In comparison, when dry pressing with hG, theoretically there is no upper limit for electrode mass loading; the high-mass-loading electrodes are as mechanically robust as, if not more mechanically robust than, the lower loading ones.

The fabrication of hG electrodes via a continuous dry-pressing process similar to conventional slurry casting should be a viable approach to achieving high throughput. Currently, all electrode discs are individually fabricated in our laboratories via a hydraulic press at pressures of up to 500 MPa. However, the pressure for robust disc formation can be as low as 20 MPa, a

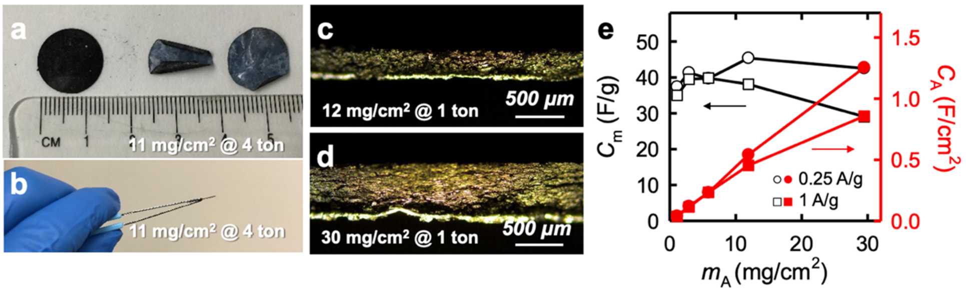


Figure 4. Dry-pressed neat hG electrodes for supercapacitors. (a, b) Photographs of a freestanding 20 mg (or 11 mg/cm^2) hG disc (to the right are the Celgard separation films that were peeled off) from the dry pressing of an hG powder sample at 4 ton. (c, d) Optical micrographs of cross sections of hG electrodes from dry pressing at 1 ton weighed at ∼21 and ∼52 mg (or ∼12 and ∼30 mg/cm^2), respectively. The shiny layer at the bottom of each cross section was the Al foil piece that was left attached. (e) Relationships of gravimetric (C_m, black) and areal (C_A, red) capacitances, respectively, vs electrode mass loading (m_A) at current densities of 0.25 and 1 A g^{-1}. Reproduced with permission from ref 28. Copyright 2016 American Chemical Society.

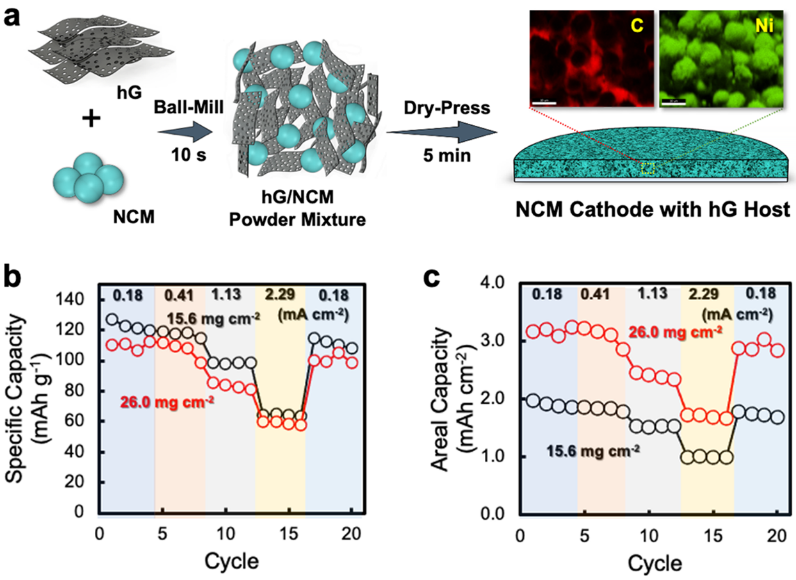


Figure 5. Dry-pressed composite electrodes for Li ion batteries. (a) Schematic illustration of mixing hG and NCM powder via a short ball-mill process, followed by dry pressing into a composite hG/NCM cathode. The C and Ni elemental maps of the electrode cross-section are shown (scale bars = 10 μm). (b) and (c) show the same data but plotted them with (b) specific and (c) areal capacity values at discharge, respectively. These Li-NCM cells contained dry-pressed hG/NCM cathodes with NCM mass loadings of 15.6 mg cm^{-2} (black) and 26.0 mg cm^{-2} (red). Reproduced with permission from ref 30. Copyright 2020 Elsevier.

value that is equivalent to what is typically used in conventional roll-to-roll (R2R) calendaring.[29,30] Therefore, it is conceivable that the hG-based dry-press electrode fabrication method can be scaled up by using a dry R2R manufacturing approach (Figure 3c), in which loose hG-based powder may be placed onto either a preset mold on a conveyer belt or onto the desired current collector and subjected to similar hydraulic pressure at the roller already used in conventional R2R electrode manufacturing.

4. APPLICATIONS OF DRY-PRESSED HOLEY GRAPHENE ELECTRODES

4.1. Neat Holey Graphene Electrodes for Supercapacitors

Neat hG electrodes were obtained by dry-pressing hG by itself and were tested for supercapacitor (or “ultracapacitor”) performance.[28] Supercapacitors are high-power electrochemical energy storage systems via electrical double-layer formation for which conductive carbons with high surface area are ideal electrode choices.[38] Carbon nanomaterials such as carbon nanotubes or graphene, because of their high electrical conductivity and high surface area, have attracted tremendous attention in supercapacitor applications, which nearly dominated the initial explorations of these novel materials in the energy storage field.[18,19,38]

Commercial supercapacitor cells with electrodes made with activated carbon typically limit the material loading to around 10 mg cm^{-2}.[39] Besides fabrication challenges with the slurry-based method, gravimetric capacitance beyond this loading level is considered to be ineffective because of much impeded ion transport through the electrode thickness (typically ∼100 μm). In comparison, the dry-press method allowed the facile fabrication of neat hG electrodes with mass loadings of as high as 30 mg cm^{-2} and thicknesses of >450 μm (Figure 4a−d).[28] Impressively, the gravimetric capacitance of the dry-pressed hG electrodes remained nearly constant over the entire 1−30 mg cm^{-2} range at current densities of up to 1 A g^{-1}. The areal capacitance, which is the measure of energy storage in a unit device footprint, increased proportionally to the mass loading and reached 1.25 and 0.86 F cm^{-2} at 0.25 and 1 A g^{-1}, respectively (Figure 4e). These values were among the highest

https://doi.org/10.1021/acs.accounts.2c00457
Acc. Chem. Res. 2022, 55, 3020−3031

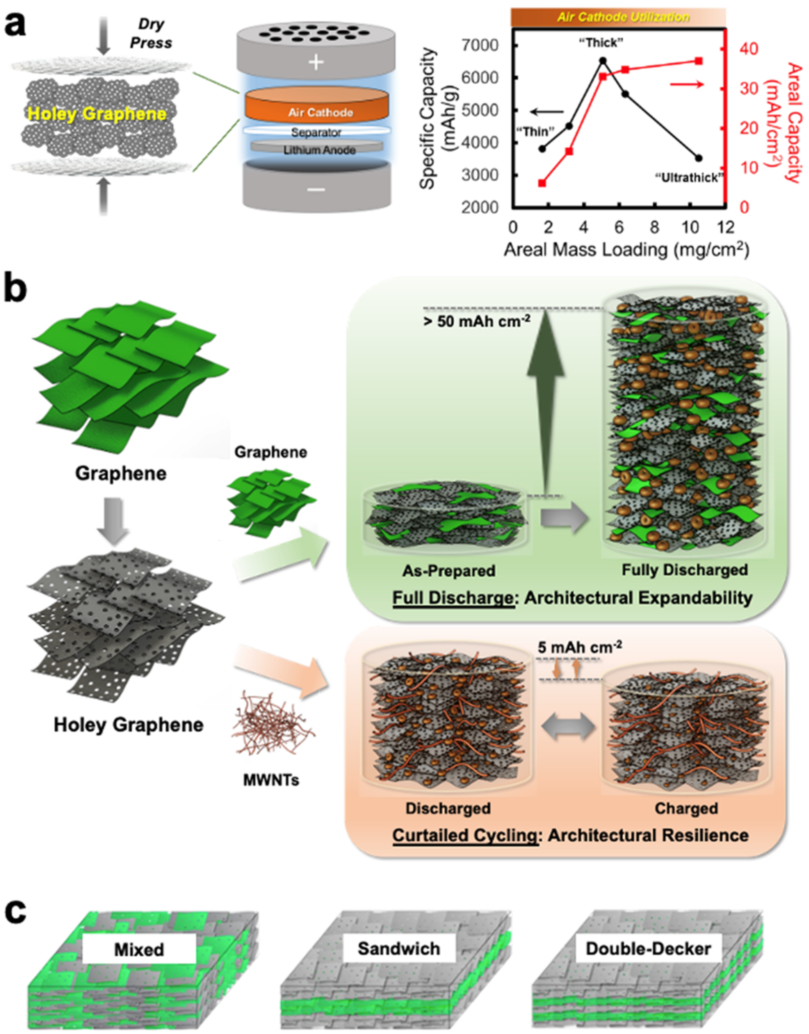


Figure 6. Dry-pressed neat and composite air cathodes for Li−O_2 batteries. (a) (Left) Schematic of a typical Li−O_2 coin cell in which the air cathode is made by dry pressing neat hG powder. (Right) Dependence of specific (left axis) and areal (right axis) capacities on the mass loading of dry-pressed hG air cathodes. Reproduced with permission from ref 34. Copyright 2017 American Chemical Society. (b) Cartoon illustrations (not drawn to scale) showing architectural transformations of (top) an hG/graphene composite air cathode under full discharge and (bottom) an hG/MWNT (MWNT stands for multiwalled carbon nanotube) composite air cathode under curtailed cycling conditions. Reproduced with permission from ref 37. Copyright 2021 Wiley-VCH. (c) Cartoon illustrations (not drawn to scale) of dry-pressed hG-based air cathode embedded catalysts (green color) to form (left) mixed, (middle) sandwich, and (right) double-decker architectures. Reproduced with permission from ref 35. Copyright 2017 Elsevier.

achieved at the time of the report. There have been reports on achieving high area capacities using 3D electrode architectures.[40] However, these electrodes may not be ideal volumetrically in comparison to much more compacted dry-pressed hG electrodes, which may also have potential applications in microsupercapacitors.[41]

4.2. Composite Electrodes for Li Ion Batteries

Li ion batteries take advantage of the reversible intercalation of Li ions into layered compounds at the cathode.[42] Recently, intensive research efforts have sought to replace the conventional graphite anode with Li metal to significantly improve the energy density.[43] To effectively pair with such a high energy density anode, the fabrication of a high-mass-loading cathode is imperative. Various Li-containing compounds, such as lithium iron phosphate (LFP) and lithium nickel manganese cobalt oxide (NMC or NCM), have been used as cathodic active materials in Li ion batteries. Although carbon additives such as carbon black are usually required to improve the conductivity of the Li ion battery cathodes, the use of hG as a conductive additive enables the fabrication of the composite cathodes via facile dry compression, similar to the neat hG electrodes.[29,30]

Li ion cathode composite discs were conveniently fabricated by compressing a powder mixture of hG and any desirable Li ion battery cathodic materials (Figure 5a). Because hG is a much lighter material (∼0.7−1 g cm^{-3} for neat hG after compression) in comparison to most Li ion cathode materials (>2 g cm^{-3}), only a small weight fraction of hG is needed in the composite mixture to provide sufficient volumetric accommodation to enable dry compression. For example, hG/NCM composite discs with up to 90 wt % NCM, or only 10 wt % hG, were conveniently prepared from the corresponding powdery mixture.[30]

The compression pressure used with a hydraulic press for successful disc fabrication could be as low as 20 MPa, a value that is achievable in typical R2R dry powder calendaring equipment. At such a low fabrication pressure, the composite cathodes with LFP or NCM both exhibited excellent performance. For example, an hG/LFP (50 wt % LFP) cathode[29] and an hG/NCM (90 wt % NCM) cathode[30] exhibited first charge capacities of >160 mAh g^{-1} at 0.2 C and ~230 mAh g^{-1} at 0.18 mA cm^{-2}, at high mass loadings of 11.6 and 15.6 mg cm^{-2}, respectively. One of the major advantages of hG-enabled dry-press fabrication is that ultrahigh mass loading electrodes could be fabricated with the exact same process in the same amount of time (a few minutes). An hG/NCM cathode with a mass loading of as high as 26 mg cm^{-2} was fabricated and exhibited only a slight reduction in gravimetric capacity (110 vs 127 mAh g^{-1}) but significantly enhanced areal performance (3.2 vs 2.0 mAh cm^{-2}) in comparison to the one with a relatively lower mass loading of 15.6 mg cm^{-2} (Figure 5b,c).[30] The performances of some of the recently reported high-mass-loading NCM cathodes are compared with that of the dry-pressed hG/NCM cathodes in Supporting Information Table S1.

4.3. Neat and Composite Air Cathodes and Architectures for Li−O_2 Batteries

In nonaqueous Li−O_2/air batteries, the true cathodic reagent is the gaseous O_2 molecules from the atmosphere in contact with the Li^+-containing electrolyte in the cathodic compartment.[44,45] The discharge reaction generates insoluble Li_2O_2 particles, which decompose during charge in the reverse electrochemical reaction. As such, the primary functions of this compartment, or the air cathode, are more than just current collectors to conduct electrons but also an architectural scaffold to accommodate the growth and decomposition processes of insoluble discharge products. Carbon nanomaterials such as carbon nanotubes and graphene are electrically conductive, porous, and lightweight and therefore are the most popular choices as the air cathode materials.[46,47]

In the current literature, extraordinary carbon-based gravimetric capacitance (>20 000 mAh g_C^{-1}) has been reported,[44,45] but the amount of carbon used for the air cathode has been low (~0.1−1 mg cm^{-2}), resulting in low full areal capacitance (<5−10 mAh cm^{-2}). In addition, a major focus in current Li−O_2/air battery research is the development of electrocatalysts for the charge reaction in order to improve cyclability, for which significant progress has indeed been made. However, because the large insoluble Li_2O_2 particles exhibit sluggish decomposition during charging, cycling studies are usually conducted at a much lower "curtailed" value, typically 1000 mAh g^{-1} (equivalent to 1 mAh cm^{-2} if accompanied by 1 mg cm^{-2} loading). Such values are far from satisfactory for Li−O_2/air batteries to be a competitive energy-storage platform.

The use of dry-pressed, high-mass-loading hG air cathodes provides a novel perspective for air cathode materials beyond their conductive and catalytic functions, but with added emphasis on their role as an architectural scaffold. Although low-mass-loading air cathodes may be used to study electrochemical and catalytic reaction mechanisms, the total surface area or pore volume is insufficient and only a small amount of discharge product Li_2O_2 can be formed. In comparison, dry-pressed neat hG electrodes (Figure 6a) have a high carbon mass loading (5−10 mg cm^{-2}) with a large total pore volume and a robust percolating network that allowed the accommodation of an extraordinary quantity of discharge products while remaining electrochemically viable. The result was ultrahigh-areal-capacity values of up to 40 mAh cm^{-2}, forming toroid-shaped Li_2O_2 particles as large as 1 μm in diameter upon full discharge.[34]

In an effort to reveal the mechanism of such ultrahigh areal capacity and whether further improvement can be made, all-carbon composite air cathodes were fabricated using hG as the dry-press host matrix but with other carbon materials as fillers (with a weight ratio of 5:1).[37] Interestingly, almost all of the carbon material fillers, including carbon black, carbon nanotubes, and chemically reduced graphene (c-G), reduced the full discharge capacity, with some by as much as 70%. This was despite the same amount of total carbon used and similar chemical and physical characteristics (i.e., density, surface area, surface conductivity, and oxygen content) of the dry-pressed composite electrode discs. The only exception was the use of thermally reduced graphene (t-G), the starting intact graphene material for hG, that improved the capacitance by ~10% (to a record value of 53 mAh cm^{-2}). t-G is the only material that would exhibit more volume rebound after dry compression than hG, as previously discussed in Section 2 (Figure 2b), and thus may be able to accommodate more discharge products in the composite disc without failing. In comparison, all of the other carbon additives disrupted the expandable scaffolding, resulting in a capacity reduction. It was thus postulated that the air cathode structural volume expandability was the key to withstanding extraordinary volume expansion enabling ultrahigh areal capacity while maintaining electrochemical integrity (Figure 6b).

In cycling studies, a typical capacity curtailing strategy was used, in which the high-mass-loading hG-based cathodes were cycled at a designated capacity of 2 or 5 mAh cm^{-2}, despite their ultrahigh full discharge capacity values.[37] For hG, the total capacity output (curtailed capacity × number of cycles) barely improved from the full discharge value. However, the use of carbon nanotube additives significantly improved the cyclability of the dry-pressed composite discs, although they performed poorly in full discharge. Because of the much smaller volume change during curtailed cycling, the architectural resilience induced by the nanotube fillers, or the "breathability" of the air cathode, was believed to be crucial in improved cyclability. The architectural expandability and breathability of ultrahigh-areal-capacity air cathodes (Figure 6b) are novel concepts in the field of Li−O_2 batteries and will require more quantitative evaluations in future studies.

Heterogeneous electrocatalysts,[44,45] a key air cathode additive for enhanced cyclability, may also be conveniently incorporated into dry-pressed hG electrodes. In a concept study, a Ni-based electrocatalyst was embedded in the hG matrix and pressed into composite discs as a mixture or in a layerwise fashion (Figure 6c).[35] For the latter, composite electrodes with either sandwich-like or double-decker architectures were successfully fabricated and exhibited similar stable cycling performance at a high curtailing capacity (4 mAh cm^{-2}). Such designed architectures may enable further mechanistic investigations into Li−O_2 electrocatalytic chemistry in thick electrodes.[48]

Soluble catalysts, or redox mediators (RMs), were also explored with the high-mass-loading hG air cathode platform.[36] Unlike heterogeneous electrocatalysts which are typically metal-containing compounds, the RMs are small ions or molecules that are soluble in the electrolyte and thus much more effective in accessing the insoluble discharge products to improve the charge reaction. However, also because they are soluble, previous studies showed that parasitic events readily occur such as shuttling through the separator to react with the Li anode. This effect was amplified when a high cycling areal capacity (2 mAh cm^{-2}) was applied by using dry-pressed, high-mass-loading neat hG electrodes despite much improved cyclability (48 cycles with vs 29 cycles without LiI as RM; mass loading 10 mg cm^{-2}). Under this condition, the redox activity from the I_3^-/I_2 pair was identified, and the depletion of LiI through shuttling was

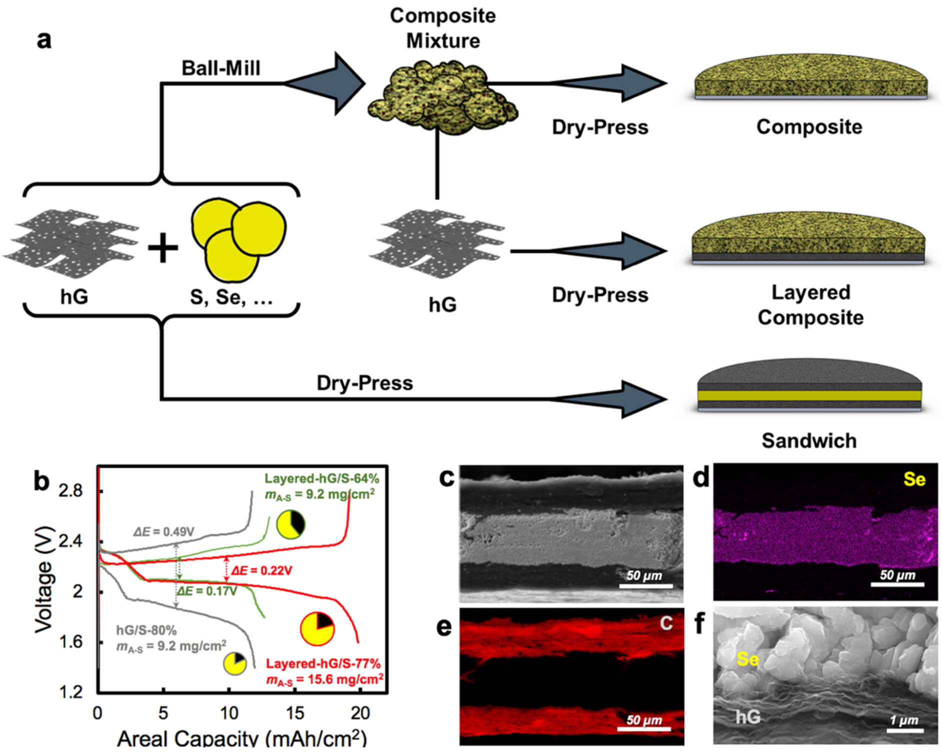


Figure 7. Dry-pressed composite cathodes for Li−S/Se batteries. (a) Schematics showing the fabrication procedures for S/Se cathodes with (top) regular mixed composite architecture, (middle) a layered composite architecture with an additional hG interlayer for improved electrical contact with the current collector, and (bottom) a sandwich architecture where the neat active materials are directly used in the one-step dry-press process. (b) First cycles of Li−S cells with various cathodes (x% indicates the S content in the electrode): hG/S-80% with no interlayer (S mass loading $m_{A\text{-}S} = 9.2$ mg/cm^2), layered-hG/S-64% ($m_{A\text{-}S} = 9.2$ mg/cm^2), and layered-hG/S-77% ($m_{A\text{-}S} = 15.6$ mg/cm^2). The latter two electrodes with hG interlayers exhibited a significantly reduced overpotential with ultrahigh areal capacities. Reproduced with permission from ref 31. Copyright 2019 Wiley-VCH. (c−f) SEMs of a dry-pressed hG/Se/hG sandwich electrode. (c−e) Typical SEM image and the corresponding elemental maps of the cross-section of a sandwich electrode. (f) Higher-magnification view of the Se−hG interface at the cross-section. Reproduced with permission from ref 32. Copyright 2020 American Chemical Society.

quantitatively measured from the cycling data. This study unambiguously revealed that, with the shuttling-induced RM starvation, strategies to retain RMs within the cathodic compartment must be developed for practical high-areal-capacity Li−O_2 batteries.

4.4. Composite and Sandwich Cathodes for Li−S/Se Batteries

Li−S batteries are one of the highest energy density platforms (theoretical capacity 1672 mAh $g^{-1}{}_S$) with fewer parasitic side reactions than Li−O_2/air batteries and thus with more reversible electrochemistry.[49] With the low cost of S, it has attracted increased attention recently. There remain many challenges for the S cathode, such as the shuttling of soluble polysulfide intermediates and the lack of high rate performance because of the insulating nature of S. Using carbon nanomaterials and polar compounds has been a viable strategy for entrapping polysulfides, and using solid electrolytes could remove the mobility of the intermediates entirely. It was also found that the addition of Se to the S structure (i.e., Se−S compounds) may improve the rate performance significantly with little sacrifice of the energy density because Se is a much more electrically conductive material than S (10^{-5} vs 10^{-30} S cm^{-1}) with a reasonable theoretical capacity (675 mAh $g^{-1}{}_{Se}$).[50] In this regard, Li−S and Li−Se pairs may be considered to be the high-energy and high-power ends within a broad spectrum of the Li−S/Se electrochemical family, respectively, and the S−Se compounds with various S/Se ratios may be used to balance the energy and power outputs of the battery electrochemistry.

A high S/Se mass loading is essential for practical applications. For example, it was suggested that at least 5 mg cm^{-2} S loading is required to achieve the necessary energy density at the pack level.[51] However, the conventional slurry coating method has proven challenging in preparing high-mass-loading S electrodes. Not only are multiple iterations usually needed to obtain a sufficient electrode thickness, but the resultant electrodes also tend to crack or easily fail during cycling. We demonstrated that composite powder mixtures of S/Se and hG are easily compressible, with S/Se content of as high as 90% (Figure 7a).[31,33] At a high S mass loading of 6 mg cm^{-2}, a high capacity of 1429 mAh $g^{-1}{}_S$ was achieved, corresponding to 85% S utilization and an areal capacity of 8.2 mAh cm^{-1}.[31] hG/Se composite cathodes exhibited a similarly high utilization rate.[33]

The poor contact between the composite cathode and the current collector became a significant issue for ultrahigh-mass-loading S cathodes with high S contents. For example, at a S loading of 9.2 mg cm^{-2} and a content of 80%, despite the ultrahigh areal capacity achieved (∼12 mAh cm^{-2}), the overpotential from discharge/charge was quite large (0.49 V), indicating ineffective conductive paths (Figure 7b). It was found that adding a lightweight layer of dry-pressed hG between the current collector and the composite cathode significantly lowered the overpotential with retained areal performance.[31] For example, at an ultrahigh S loading of 15.6 mg cm^{-2} and a total content of 77% (considering the added hG layer), the overpotential was reduced to only 0.22 V with an areal capacity of ~20 mAh cm^{-2}. The lightweight hG interlayer (shown as the "layered composite" in Figure 7a) was the key to improving the contact conductance and therefore the electrochemical kinetics of the battery reactions.

Dry compressible hG even enabled the incorporation of neat Se in between two layers of hG, resulting in sandwichlike electrodes (Figure 7a,c).[32] This was achieved via a single-step dry compression without even the need for premixing. High-mass-loading hG|Se|hG sandwich electrodes could be conveniently fabricated just by sequentially adding hG, neat Se, and hG powders to the compression die, followed by pressing into electrodes that were directly used for battery cell fabrication. These sandwich electrodes exhibited high performance similar to that of the composite electrodes. The sandwiched neat Se was shown to electrochemically redistribute throughout the entire cathode upon the first cycle as Se was converted into soluble polyselenides during the first discharge. As such, the first cycling step was a de facto mixing process resulting in a well-mixed hG/Se composite electrode. The method was shown to be widely applicable to the S/Se family of active materials, including Se, S, and a commercially available SeS_2 compound, all of which exhibited excellent performance in terms of areal capacity and utilization. The entrapment of soluble polysulfide/polyselenide intermediates is important to improving the cyclability of Li−S/Se batteries. We have found some success in using fluorinated electrolyte solvents[32] or metal sulfide species[33] with dry-pressed hG-based electrodes. Future studies may include the direct modification of hole-edge functionalities of hG, which might provide further improvements in entrapping the soluble intermediates and thus the cycling performance.

5. CONCLUSIONS AND PERSPECTIVES

As a graphene derivative, the holey motif of hG renders to these 2D nanosheets an insignificant increase in defects but improved properties especially in terms of through-sheet mass transport. This characteristic is particularly useful in the field of energy storage, where reduced ion tortuosity leads to much enhanced performance. The holey nature of hG also makes the dry powder compressible into neat monoliths or composite architectures with electrochemically active fillers that can be directly used as a supercapacitor or battery electrodes. The dry-pressed neat and composite electrodes enabled by hG have found broad applications in advanced battery research. The use of a solvent-free and binder-free dry-press method with hG has enabled the facile preparation of high-mass-loading electrodes with the high areal capacity required for practical battery systems. In comparison, the conventional slurry-based electrode fabrication approach is time-consuming and may pose environmental concerns, with significant challenges in increasing the active material mass loading. In most cases, hG serves as not only a conductive additive but also an architectural scaffold with binder-like properties in these dry-pressed electrodes. With scalable preparation techniques available, hG may be one of the most promising carbon material candidates with advantages in both fabrication and performance for future high-energy-density battery electrodes.

A few of the challenges that need further research are listed as follows:

(1) The preparation of hG should be further improved and tailored toward individual applications. Because hG can be prepared from different starting graphene materials under various oxidation conditions, its properties such as the oxygen content, hole size, original graphene defect density, and surface area may vary and could play important roles in each application. Subsequent modifications, such as inorganic or organic functionalizations and heteroatomic doping, can be critical toward specific functions.

(2) The hole-edge chemistry of hG remains to be fully understood. Although hG shares similarities with intact graphene in its chemical properties, the chemistry at the hole edges has not been fully exploited. Manipulation of the hole edge carbon chemistries will have important effects on not only graphene surface properties, but also the through-hole transport properties for energy storage applications. There are reports already available on hG hole edge modifications that impact the catalytic[24] and ion-transport properties.[52]

(3) Dry-pressed hG architectures require more fundamental understanding and improvement. For example, dry-pressed hG discs are robust but not flexible. It remains to be seen whether they could be improved and applied to flexible devices with proper modifications either within the structure or in the fabrication procedure. Dry-pressed hG-based electrodes also swell upon applying solvents or liquid electrolytes. Although they retain their excellent electrochemical viability, exhibit high areal capacity, and remain mechanically robust against repeated cycling, the swelling may pose a challenge when scaling up battery cell fabrication.

(4) Applications of dry-pressed hG need to be further explored. hG has been used in applications such as catalysis, sensing, adsorbents, membranes, and composites, for which dry-pressed hG may present a unique niche. In the energy storage field, besides what has been discussed in this Account, there are several other important areas of immediate interest, such as applications in Li metal anodes and solid-state electrodes. For the former, intact graphene has been shown to be an excellent lightweight host for Li metal to reduce dendrite formation and thus improve cyclability. Dry-pressed hG might improve the fabrication of such Li metal host electrodes. For the latter, because many solid-state cathode discs have already been prepared by dry compression, it is logical to predict that the use of hG could further facilitate the fabrication and improve the performance by enhancing the interfacial contacts among the various constituents. Both directions are actively being pursued in our laboratory.

(5) The holey motif has been explored in many other 2D nanosheets, some of which exhibited enhanced electrochemical properties.[53,54] It is intriguing to discover whether those holey nanosheets are also compressible in their dry form. Scalable preparation methods will be essential for such explorations.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.accounts.2c00457.

Preparation of holey graphene and holey graphene as an advanced alternative to graphene for energy storage (PDF)

AUTHOR INFORMATION

Corresponding Authors

Yi Lin – *Advanced Materials and Processing Branch, NASA Langley Research Center, Hampton, Virginia 23681, United States;* orcid.org/0000-0002-1828-3518; Email: yi.lin-1@nasa.gov

Liangbing Hu – *Department of Materials Science and Engineering and Center for Materials Innovation, University of Maryland, College Park, Maryland 20742, United States;* orcid.org/0000-0002-9456-9315; Email: binghu@umd.edu

Authors

Christian O. Plaza-Rivera – *NASA Interns, Fellows, and Scholars (NIFS) Program, NASA Langley Research Center, Hampton, Virginia 23681, United States*

John W. Connell – *Advanced Materials and Processing Branch, NASA Langley Research Center, Hampton, Virginia 23681, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.accounts.2c00457

Author Contributions

[‖]Retired. CRediT: **Yi Lin** conceptualization (equal), data curation (lead), funding acquisition (equal), investigation (lead), project administration (lead), writing-original draft (lead), writing-review & editing (lead); **Christian O Plaza-Rivera** data curation (supporting), investigation (supporting), writing-review & editing (supporting); **Liangbing Hu** conceptualization (equal), investigation (supporting), writing-review & editing (supporting); **John W Connell** conceptualization (equal), funding acquisition (equal), investigation (supporting), project administration (supporting), writing-review & editing (supporting).

Notes

The authors declare no competing financial interest.

Biographies

Yi Lin is a research materials engineer in the Advanced Materials and Processing Branch at NASA Langley Research Center (LaRC). He received B.S. (1996) and M.S. (1999) degrees from the University of Science and Technology of China and a Ph.D. (2004) from Clemson University. He is a recipient of the NASA Technology Achievement Medal (2017) and NASA Langley Research Center's H. J. E. Reid Award (2018). His current research interest is the synthesis and applications of low-dimensional nanomaterials, especially those useful in energy storage, electric aircraft, and space exploration.

Christian O. Plaza-Rivera received his bachelor's degree in physics from the University of Puerto Rico at Mayagüez in 2021. He is currently a materials science and engineering Ph.D. student at the Massachusetts Institute of Technology (MIT) and a research assistant at the Electrochemical Energy Laboratory (EEL), where he continues to work on the development of next-generation lithium–metal batteries.

Liangbing Hu is a Herbert Rabin Distinguished Professor at the University of Maryland (UMD), College Park and the director of the Center for Materials Innovation (CMI). He received his B.S. from the University of Science and Technology of China (USTC) and Ph.D from the University of California, Los Angeles (UCLA). His research group at UMD focuses on material innovations, device integrations, and manufacturing in general, with ongoing research activities on wood nanotechnologies, 3000 K extreme materials, and beyond Li ion batteries.

John W. Connell recently (December 2021) retired from the Advanced Materials and Processing Branch at the NASA Langley Research Center where he worked for ~35 years. He received B.S. (1982 chemistry) and Ph.D. (1986 organic/polymer chemistry) degrees from Virginia Commonwealth University. He received the prestigious NASA Medal for Exceptional Scientific Achievement in 1997, the Co-Inventor Commercial Invention of the Year Award for NASA in 2008, and Exceptional Technology Achievement Medal in 2015. He is Editor-in-Chief of *High Performance Polymers Journal* and a fellow of both the Institute of Physics and the Society for the Advancement of Material and Process Engineering (SAMPE).

ACKNOWLEDGMENTS

Financial support from the NASA Langley Internal Research and Development (IRAD) Program and the NASA Convergent Aeronautics Solutions (CAS) program is gratefully acknowledged. We thank E. Walsh, S. Lacey, C. Buelke, B. Moitoso, C. Martinez-Martinez, E. Hitz, N. Delumpa-Alexander, F. Mendez Sosa, L. Greenburg, B. Clifford, and B. Walker for their experimental contributions. Dr. K. Watson and Dr. J.-W. Kim were instrumental in the early development of holey graphene materials and applications. We also thank Prof. Liming Dai (University of New South Wales, Australia) for fruitful collaborations while he was at Case Western Reserve University, USA. Thanks also go to Prof. Veronica Barone (Central Michigan University), Prof. Teng Li (University of Maryland, College Park), and Dr. Wenquan Lu (Argonne National Laboratory) for their collaborations and enlightening discussions.

REFERENCES

(1) Georgakilas, V.; Perman, J. A.; Tucek, J.; Zboril, R. Broad Family of Carbon Nanoallotropes: Classfication, Chemistry, and Applications of Fullerenes, Carbon Dots, Nanotubes, Graphene, Nanodiamonds, and Combined Superstructures. *Chem. Rev.* **2015**, *115*, 4744–4822.

(2) Allen, M. J.; Tung, V. C.; Kaner, R. B. Honeycomb Carbon: A Review of Graphene. *Chem. Rev.* **2010**, *110*, 132–145.

(3) Haddon, R. C. Graphene – The Mother of Two-Dimensional (2-D) Materials. *Acc. Chem. Res.* **2013**, *46*, 2191–2192.

(4) Zhu, Y.; James, D. K.; Tour, J. M. New Routes to Graphene, Graphene Oxide and Their Related Applications. *Adv. Mater.* **2012**, *24*, 4924–4955.

(5) Georgakilas, V.; Otyepka, M.; Bourlinos, A. B.; Chandra, V.; Kim, N.; Kemp, K. C.; Hobza, P.; Zboril, R.; Kim, K. S. Functionalization of Graphene: Covalent and Non-Covalent Approaches, Derivatives and Applications. *Chem. Rev.* **2012**, *112*, 6156–6214.

(6) Li, Q.; Mahmood, N.; Zhu, J.; Hou, Y.; Sun, S. Graphene and Its Composites with Nanoparticles for Electrochemical Energy Applications. *Nano Today* **2014**, *9*, 668–683.

(7) Hu, C.; Lin, Y.; Connell, J. W.; Cheng, H.-M.; Gogotsi, Y.; Titirici, M.-M.; Dai, L. Carbon-Based Metal-Free Catalysts for Energy Storage and Environmental Remediation. *Adv. Mater.* **2019**, *31*, 1806128.

(8) Lin, Y.; Liao, Y.; Chen, Z.; Connell, J. W. Holey Graphene: A Unique Structural Derivative of Graphene. *Mater. Res. Lett.* **2017**, *5*, 209–234.

(9) Dutta, D.; Jiang, J.-Y.; Jamaluddin, A.; He, S.-M.; Hung, Y.-H.; Chen, F.; Chang, J.-K.; Su, C.-Y. Nanocatalyst-Assisted Fine Tailoring of Pore Structure in Holey-Graphene for Enhanced Performance in Energy Storage. *ACS Appl. Mater. Interfaces* **2019**, *11*, 36560–36570.

(10) Guirguis, A.; Maina, J. W.; Kong, L.; Henderson, L. C.; Rana, A.; Li, L. H.; Majumder, M.; Dumee, L. F. Perforation Routes towards Practical Nano-Porous Graphene and Analogous Materials Engineering. *Carbon* **2019**, *155*, 660−673.

(11) Chen, Z.; An, X.; Dai, L.; Xu, Y. Holey Graphene-Based Nanocomposites for Efficient Electrochemical Energy Storage. *Nano Energy* **2020**, *73*, 104762.

(12) Lin, Y.; Watson, K. A.; Kim, J.-W.; Baggett, D. W.; Working, D. W.; Connell, J. W. Bulk Preparation of Holey Graphene via Controlled Catalytic Oxidation. *Nanoscale* **2013**, *5*, 7814−7824.

(13) Han, X.; Funk, M. R.; Shen, F.; Chen, Y.-C.; Li, Y.; Campbell, C. J.; Dai, J.; Yang, X.; Kim, J.-W.; Liao, Y.; Connell, J. W.; Barone, V.; Chen, Z.; Lin, Y.; Hu, L. Scalable Holey Graphene Synthesis and Dense Electrode Fabrication toward High-Performance Ultracapacitors. *ACS Nano* **2014**, *8*, 8255−8265.

(14) Lin, Y.; Han, X.; Campbell, C. J.; Kim, J.-W.; Zhao, B.; Luo, W.; Dai, J.; Hu, L.; Connell, J. W. Holey Graphene Nanomanufacturing: Structure, Composition, and Electrochemical Properties. *Adv. Funct. Mater.* **2015**, *25*, 2920−2927.

(15) Zhao, X.; Hayner, C. M.; Kung, M. C.; Kung, H. H. In-Plane Vacancy-Enabled High-Power Si-Graphene Composite Electrode for Lithium-Ion Batteries. *Adv. Energy Mater.* **2011**, *1*, 1079−1084.

(16) Xu, Y.; Lin, Z.; Zhong, X.; Huang, X.; Weiss, N. O.; Huang, Y.; Duan, X. Holey Graphene Frameworks for Highly Efficient Capacitive Energy Storage. *Nat. Commun.* **2014**, *5*, 4554.

(17) Zhao, Y.; Hu, C.; Song, L.; Wang, L.; Shi, G.; Dai, L.; Qu, L. Functional Graphene Nanomesh Foam. *Energy Environ. Sci.* **2014**, *7*, 1913−1918.

(18) El-Kady, M. F.; Shao, Y.; Kaner, R. B. Graphene for Batteries, Supercapacitors and Beyond. *Nat. Rev. Mater.* **2016**, *1*, 16033.

(19) Huang, H.; Shi, H.; Das, P.; Qin, J.; Li, Y.; Wang, X.; Su, F.; Wen, P.; Li, S.; Lu, P.; Liu, F.; Li, Y.; Zhang, Y.; Wang, Y.; Wu, Z.; Cheng, H.-M. The Chemistry and Promising Applications of Graphene and Porous Graphene Materials. *Adv. Funct. Mater.* **2020**, *30*, 1909035.

(20) Xu, J.; Lin, Y.; Connell, J. W.; Dai, L. Nitrogen-Doped Holey Graphene as Anode for Lithium Ion Batteries with High Volumetric Density and Long Cycle Life. *Small* **2015**, *11*, 6179−6185.

(21) Shui, J.; Lin, Y.; Connell, J. W.; Xu, J.; Fan, X.; Dai, L. Nitrogen-Doped Holey Graphene for High-Performance Rechargeable Li-O_2 Batteries. *ACS Energy Lett.* **2016**, *1*, 260−265.

(22) Qie, L.; Lin, Y.; Connell, J. W.; Xu, J.; Dai, L. Highly Rechargeable Lithium-CO_2 Batteries with a Boron and Nitrogen-Codoped Holey-Graphene Cathode. *Angew. Chem. Int. Ed* **2017**, *56*, 6970−6974.

(23) Jin, Y.; Hu, C.; Dai, Q.; Xiao, Y.; Lin, Y.; Connell, J. W.; Chen, F.; Dai, L. High-performance Li-CO_2 Batteries Based on Metal-free Carbon Quantum Dot/Holey Graphene Composite Catalysts. *Adv. Funct. Mater.* **2018**, *28*, 1804630.

(24) Hu, C.; Gong, L.; Xiao, Y.; Yuan, Y.; Bedford, N.; Xia, Z.; Ma, L.; Wu, T.; Lin, Y.; Connell, J. W.; Shahbazian-Yassar, R.; Lu, J.; Amine, K.; Dai, L. High-Performance, Long-Life, Rechargeable Li-CO_2 Batteries based on a 3D Holey Graphene Cathode Implanted with Single Iron Atoms. *Adv. Mater.* **2020**, *32*, 1907436.

(25) Lacey, S. D.; Kirsch, D. J.; Li, Y.; Morgenstern, J. T.; Zarket, B. C.; Yao, Y.; Dai, J.; Garcia, L. Q.; Liu, B.; Gao, T.; Xu, S.; Raghavan, S. R.; Connell, J. W.; Lin, Y.; Hu, L. Extrusion-Based 3D Printing of Hierarchically Porous Advanced Battery Electrodes. *Adv. Mater.* **2018**, *30*, 1705651.

(26) Han, X.; Yang, Z.; Zhao, B.; Zhu, S.; Zhou, L.; Dai, J.; Kim, J.-W.; Liu, B.; Connell, J. W.; Li, T.; Yang, B.; Lin, Y.; Hu, L. Compressible, Dense, Three-Dimensional Holey Graphene Monolithic Architecture. *ACS Nano* **2017**, *11*, 3189−3197.

(27) Kraytsberg, A.; Ein-Eli, Y. Conveying Advanced Li-Ion Battery Materials into Practice the Impact of Electrode Slurry Preparation Skills. *Adv. Energy Mater.* **2016**, *6*, 1600655.

(28) Walsh, E. D.; Han, X.; Lacey, S. D.; Kim, J.-W.; Connell, J. W.; Hu, L.; Lin, Y. Dry-Processed, Binder-Free Holey Graphene Electrodes for Supercapacitors with Ultrahigh Areal Loadings. *ACS Appl. Mater. Interfaces* **2016**, *8*, 29478−29485.

(29) Kirsch, D. J.; Lacey, S. D.; Kuang, Y.; Pastel, G.; Xie, H.; Connell, J. W.; Lin, Y.; Hu, L. Scalable Dry Processing of Binder-free Lithium-ion Battery Electrodes Enabled by Holey Graphene. *ACS Appl. Energy Mater.* **2019**, *2*, 2990−2997.

(30) Walker, B. A.; Plaza-Rivera, C. O.; Sun, S.-S.; Lu, W.; Connell, J. W.; Lin, Y. Dry-Pressed, High Mass Loading, Lithium Nickel Cobalt Manganese Oxide (NCM) Cathodes Enabled by Holey Graphene Host. *Electrochim. Acta* **2020**, *362*, 137129.

(31) Lin, Y.; Jones, K. J.; Greenburg, L. C.; Kim, J.-W.; Hu, L.; Connell, J. W. Facile, Solvent-Free Preparation of High Density, High Mass Loading Sulfur Cathodes Enabled by Dry-Pressible Holey Graphene Scaffolds. *Batteries & Supercaps* **2019**, *2*, 774−783.

(32) Plaza-Rivera, C. O.; Walker, B. A.; Tran, N. X.; Viggiano, R. P.; Dornbusch, D. A.; Wu, J. J.; Connell, J. W.; Lin, Y. Dry Pressing Neat Active Materials into Ultrahigh Mass Loading Sandwich Cathodes Enabled by Holey Graphene Scaffold. *ACS Appl. Energy Mater.* **2020**, *3* (7), 6374−6382.

(33) Plaza-Rivera, C. O.; Viggiano, R. P.; Dornbusch, D. A.; Wu, J. J.; Connell, J. W.; Lin, Y. Holey Graphene−Enabled Solvent-Free Preparation of Ultrahigh Mass Loading Selenium Cathodes for High Areal Capacity Lithium−Selenium Batteries. *Front. Energy Res.* **2021**, *9*, 703676.

(34) Lin, Y.; Moitoso, B.; Martinez-Martinez, C.; Walsh, E. D.; Lacey, S. D.; Kim, J.-W.; Dai, L.; Hu, L.; Connell, J. W. Ultrahigh-Capacity Lithium-Oxygen Batteries Enabled by Dry-Pressed Holey Graphene Air Cathodes. *Nano Lett.* **2017**, *17*, 3252−3260.

(35) Lacey, S. D.; Walsh, E. D.; Hitz, E.; Dai, J.; Connell, J. W.; Hu, L.; Lin, Y. Highly Compressible, Binderless and Ultrathick Holey Graphene-Based Electrode Architectures. *Nano Energy* **2017**, *31*, 386−392.

(36) Lin, Y.; Martinez-Martinez, C.; Kim, J.-W.; Connell, J. W. Shuttling Induced Starvation of Redox Mediators in High Areal Capacity Rechargeable Lithium-Oxygen Batteries. *J. Electrochem. Soc.* **2020**, *167*, 080522.

(37) Greenburg, L. C.; Plaza-Rivera, C. O.; Kim, J.-W.; Connell, J. W.; Lin, Y. Architecture Transformations of Ultrahigh Areal Capacity All-Carbon Air Cathodes for Lithium-Oxygen Batteries. *Batteries Supercaps* **2021**, *4*, 120−130.

(38) Simon, P.; Gogotsi, Y. Materials for Electrochemical Capacitors. *Nat. Mater.* **2008**, *7*, 845−854.

(39) Simon, P.; Gogotsi, Y. Capacitive Energy Storage in Nanostructured Carbon-Electrolyte Systems. *Acc. Chem. Res.* **2013**, *46*, 1094−1103.

(40) Chang, J.-H.; Hung, Y.-H.; Luo, X.-F.; Huang, C.-H.; Jung, S.; Chang, J.-K.; Kong, J.; Su, C.-Y. The Hierarchical Porosity of a Three-Dimensional Graphene Electrode for Binder-Free and High Performance Supercapacitors. *RSC Adv.* **2016**, *6*, 8384−8394.

(41) Chih, J.-K.; Jamaluddin, A.; Chen, F.; Chang, J.-K.; Su, C.-Y. High Energy Density of All-Screen-Printable Solid-State Microsupercapacitors Integrated by Graphene/CNTs as Hierarchical Electrodes. *J. Mater. Chem. A* **2019**, *7*, 12779−12789.

(42) Manthiram, A. A Reflection on Lithium-Ion Battery Cathode Chemistry. *Nat. Commun.* **2020**, *11*, 1550.

(43) Lin, D.; Liu, Y.; Cui, Y. Reviving the Lithium Metal Anode for High-Energy Batteries. *Nat. Nanotechnol* **2017**, *12*, 194−206.

(44) Lu, J.; Li, L.; Park, J.-B.; Sun, Y.-K.; Wu, F.; Amine, K. Aprotic and Aqueous Li-O_2 Batteries. *Chem. Rev.* **2014**, *114*, 5611−5640.

(45) Kwak, W.-J.; Rosy; Sharon, D.; Xia, C.; Kim, H.; Johnson, L. R.; Bruce, P. G.; Nazar, L. F.; Sun, Y.-K.; Frimer, A. a.; Noked, M.; Freunberger, S. A.; Aurbach, D. Lithium-Oxygen Batteries and Related Systems: Potential, Status, and Future. *Chem. Rev.* **2020**, *120*, 6626−6683.

(46) Zhang, T.; Zhou, H. From Li-O_2 to Li-Air Batteries: Carbon Nanotubes/Ionic Liquid Gels with a Tricontinuous Passage of Electrons, Ions, and Oxygen. *Angew. Chem. Int. Ed* **2012**, *51*, 11062−11067.

(47) Xiao, J.; Mei, D.; Li, X.; Xu, W.; Wang, D.; Graff, G. L.; Bennett, W. D.; Nie, Z.; Saraf, L. V.; Aksay, I. A.; Liu, J.; Zhang, J.-G.

Hierarchically Porous Graphene as a Lithium-Air Battery Electrode. *Nano Lett.* **2011**, *11*, 5071−5078.

(48) Gu, M.; Kim, B.-S. Electrochemistry of Multilayer Electrodes: From the Basics to Energy Applications. *Acc. Chem. Res.* **2021**, *54*, 57−69.

(49) Bruce, P. G.; Hardwick, L. J.; Abraham, K. M. Lithium-Air and Lithium-Sulfur Batteries. *MRS Bull.* **2011**, *36*, 506−512.

(50) Xu, G.-L.; Liu, J.; Amine, R.; Chen, Z.; Amine, K. Selenium and Selenium−Sulfur Chemistry for Rechargeable Lithium Batteries: Interplay of Cathode Structures, Electrolytes, and Interfaces. *ACS Energy Lett.* **2017**, *2*, 605.

(51) Bhargav, A.; He, J.; Gupta, A.; Manthiram, A. Lithium-Sulfur Batteries: Attaining the Critical Metrics. *Joule* **2020**, *4*, 285−291.

(52) Chen, X.; Feng, Z.; Gohil, J.; Stafford, C. M.; Dai, N.; Huang, L.; Lin, H. Reduced Holey Graphene Oxide Membranes for Desalination with Improved Water Permeance. *ACS Appl. Mater. Interfaces* **2020**, *12*, 1387−1394.

(53) Peng, L.; Fang, Z.; Zhu, Y.; Yan, C.; Yu, G. Holey 2D Nanomaterials for Electrochemical Energy Storage. *Adv. Energy Mater.* **2018**, *8*, 1702179.

(54) Nazarian-Samani, M.; Haghighat-Shishavan, S.; Nazarian-Samani, M.; Kashani-Bozorg, S. F.; Ramakrishna, S.; Kim, K.-B. Perforated Two-Dimensional Nanoarchitectures for Next-Generation Batteries: Recent Advances and Extensible Perspectives. *Prog. Mater. Sci.* **2021**, *116*, 100716.

https://doi.org/10.1021/acs.accounts.2c00457