An Overview of Engineered Graphene-Based Cathodes: Boosting Oxygen Reduction and Evolution Reactions in Lithium– and Sodium–Oxygen Batteries

Juan Luis Gómez Urbano,[a, b] Marina Enterría,[a] Iciar Monterrubio,[a] Idoia Ruiz de Larrañande,[b] Daniel Carriazo,[a, c] Nagore Ortiz Vitiriano,[a, c] and Teófilo Rojo*[a, b]
The depletion of fossil fuels, the rapid evolution of the global economy, and high living standards require the development of new energy-storage systems that can meet the needs of the world's population. Metal–oxygen batteries (M = Li, Na) arise, therefore, as promising alternatives to widely used lithium-ion batteries, due to their high theoretical energy density, which approaches that of gasoline. Although significant progress has been made in recent years, there are still several challenges to overcome to reach the final commercialization of this technology. One of the most limiting and challenging factors is the development of bifunctional cathodes towards oxygen reduction and evolution reactions. In this sense, graphene, which is very promising and tunable, has been widely explored by the research community as a key material for this technology. Herein, a wide literature overview is presented and analyzed with the aim of guiding future research in this field.

1. Introduction

Energy storage is a critical challenge for modern society, with batteries being the predominant technology of choice. At the end of the 20th century, lithium-ion batteries (LiBs) revolutionized the portable electronic device industry; however, the continuing growth of the LiB market exposes it to global manipulation due to limited lithium production sources (e.g., China’s expected 62% share of the world’s LiB production capacity will lead to dependency in Europe). Consequently, there has been growing interest in research focused on developing “beyond lithium” battery technologies to augment, or in certain situations replace, LiBs. In this scenario, metal–oxygen (M–O2) batteries arise as a great alternative due to their high theoretical energy density compared with that of current systems (100–265 Wh kg−1 versus 3458 Wh kg−1 based on Li2O2 and 1108 Wh kg−1 based on Na2O2). M–O2 batteries rely on the electrochemical reduction of molecular oxygen (the oxygen reduction reaction (ORR)) at the cathode surface, with the inherent advantage of a negligible amount of “dead weight”. The cycle life of these batteries is the major bottleneck towards real implementation, in which efficient charging through the oxygen evolution reaction (OER) represents a significant challenge. The reactions taking place on rechargeable M–O2 batteries vary with the metal electrodes, the type of electrolytes, the operating parameters, and the cathode material. Generally, in aprotic electrolytes, the metal anode (e.g., Li or Na) is oxidized and ions migrate to the cathode, whereas molecular oxygen is reduced (ORR) to superoxide (O2−) or peroxide (O22−) anions at the same time. These oxygen reactive species generated by the ORR combine with the metal cation and the precipitation of metal oxides occurs at the surface of the “air–cathode” during discharge [Eq. (1)]. Upon charging, the metal oxides are redissolved to perform the oxidation of the oxygen anions (OER) and subsequent deposition of the metal in the anode [Eq. (2)].

\[
\begin{align*}
M + O_2 & \rightarrow M_2O_4 \\
M_2O_4 & \rightarrow M + O_2
\end{align*}
\]  

At the beginning of the 21st century, Li–O2 batteries emerged because of their highest theoretical energy density among all M–O2 batteries. Although great achievements have been made in recent years, several drawbacks related to battery operation, such as lithium dendrite growth, side reactions, the stability of the electrolyte, and poor kinetics, have impeded their practical application. In 2012, the substitution of Li by Na emerged as a promising approach to surpass Li–O2 battery limitations. First, the substitution of Li by Na presents several advantages, such as low cost, abundance, and higher ionic conductivities. Second, the Na–O2 battery forms the superoxide discharge product (NaO2), which does not occur in the Li system, for which the peroxide product (Li2O2) is preferentially formed. The one-electron oxygen reduction thus conducted in the Na–O2 battery reduces the energy density of the battery, but greatly enhances the kinetics and reversibility of the process by delivering a suitable charge potential (lower overpotential) and coulombic efficiency. Na–O2 batteries, however, are still novel technology that requires further development before widespread commercialization is possible.

Apart from the overall cell performance, both technologies require the utilization of a suitable cathode material that is able to accommodate the maximum amount of discharge products without pore clogging and subsequent cell failure. In this sense, different strategies have been followed for the design of the air electrode. Generally, ORR/OER electrocatalysts have been utilized to improve the efficiency of the cathode, of which carbon-based materials have been most studied. Porous carbon materials have been largely used as electrodes.

\[a\] J. L. Gómez Urbano, Dr. M. Enterria, I. Monterrubio, Dr. D. Carriazo, Dr. N. Ortiz Vitoriano, Prof. T. Rojo
CIC energiGUNE, Álava Technology Park
C/ Albert Einstein 48, 01510 Miñano (Spain)
E-mail: notiz@cicenergigune.com
teo.rojo@ehu.eus

[b] J. L. Gómez Urbano, I. Ruiz de Larramendi, Prof. T. Rojo
Department of Inorganic Chemistry
University of the Basque Country UPV/EHU
P.O. Box 664, 48080, Bilbao (Spain)

[c] Dr. D. Carriazo, Dr. N. Ortiz Vitoriano
IKERBASQUE, Basque Foundation for Science
48013 Bilbao (Spain)

The ORCID identification number(s) for the author(s) of this article can be found under:
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Among carbon-based materials, graphene has been appointed as a very versatile and promising air cathode in Li–O2 batteries due to its high electronic conductivity (≈2000 S m⁻¹), specific surface area (>2600 m² g⁻¹), mechanical strength, low density, and intrinsic catalytic activity towards the ORR/OER. Consequently, graphene has found applications in different fields, such as energy conversion and storage, electronics, sensors, adsorption, or water purification. Among electrochemical energy-storage systems, graphene has been widely used in LiB anodes. Graphene can buffer the volume changes that occur during Li insertion; moreover, graphene acts not only as the ideal matrix, but also as the support, thanks to its high electronic conductivity and ability to mitigate oxide pulverization. Graphene has also been used to mitigate manganese loss from spinel lithium manganese oxide (LMO) cathodes during cycling in LiBs to improve the battery lifetime. In addition, graphene confers suitable electrode channels for O₂ diffusion, facilitates the impregnation of the electrolyte, and offers a high number of active sites for the formation/deposition and decomposition of the discharge products. However, in practical terms, effective access to the large and active 2D surface of graphene is subjected to careful engineering of both the morphology and the 3D structure. This is extremely important in M–O₂ batteries; an optimum air cathode should maximize oxygen diffusion towards the three-phase boundary (i.e., electrolyte/electrode/oxygen interface) and accommodate a large amount of discharge product during the ORR. To improve the catalytic activity of graphene in M–O₂ batteries, different routes have been explored, such as the introduction of heteroatoms into the graphene structure, the addition of transition-metal catalysts (pure metals or metal oxides), or the nanostructuring of electrode materials for increased exposure of the active sites.

Although numerous parameters play an important role in the ORR/OER kinetics, this review focuses on those related to the cathode materials and, specifically, graphene-based air cathodes in both Li/Na–O₂ batteries. Hence, we summarize the great efforts that have been dedicated within the last decade to the development of catalytic materials for overcoming sluggish kinetics during the ORR and OER. Therefore, this review has been divided into sections on pure graphene-based materials, graphene–metal composites, and heteroatom-doped or functionalized graphene.

Nagore Ortiz-Vitoriano is an Ikerbasque Research Fellow and metal–air research line manager at CIC energiGUNE (Spain). She obtained her doctorate in 2011 for her work on solid oxide fuel cells (UPV/EHU, Spain), during the course of which she undertook research stays at Risø DTU (Denmark) and Imperial College London (UK). In 2013, she was awarded a Marie Curie IOF from the EU, which enabled her to join the Massachusetts Institute of Technology (USA), where she worked on metal–air batteries. In 2015, she continued at CIC energiGUNE, where she conducted research stays at Oak Ridge National Laboratory (USA) and Deakin University (Australia).

Teófilo Rojo received his PhD in chemistry from the University of the Basque Country (Spain) in 1981. He became Full Professor of Inorganic Chemistry at the UPV/EHU in 1992. His research has been focused on solid-state chemistry and materials science. Since 2010, he has been Scientific Director of the CIC energiGUNE, developing materials research for advanced batteries. In 2015, he was appointed an academic member of the Royal Spanish Academy of Exact, Physical and Natural Sciences, and in 2016 he was named a member of the working party on chemistry and energy of EuCheMS (European Chemical Science).

2. Lithium–Oxygen Batteries

2.1. Pure graphene-based materials

Promising properties, as described in the Introduction, have pushed the research community to dedicate their efforts to study the viability of graphene air cathodes in Li–O₂ batteries (Table 1).

In this sense, graphene nanosheets (GNs) showed a much higher capacity than that of commercial carbon black (e.g., BP-2000 and Vulcan XC-72; Figure 1a), which is widely used for the manufacturing of commercial gas diffusion layers. Further studies revealed that GNs cathodes could considerably reduce the first-cycle overpotential, which could arise from the presence of vacancies and defects on the GNs surface that catalyzed the OER.

Later, Xiao et al. developed an unusual 3D graphene structure that displayed “broken egg” morphology, which was formed of shells containing numerous nanosized pores and large tunnels. The hierarchical 3D architecture with interconnected pore channels delivered an extremely high discharge capacity (15 000 mAh g⁻¹). This behavior can be ascribed to 1) numerous large tunnels, which facilitate continuous oxygen flow into the air electrode; 2) small “pores”, which provide ideal three-phase regions for the ORR, and 3) preferential nucleation of the Li₂O₂ discharge product in the vicinity of lattice defect sites.

The processing of graphene into paperlike cathodes was explored by Kim et al. through the vacuum-assisted technique by mixing GNP with graphene oxide (GO) and poly(4-styrenesulfonic acid) stabilizers. GNP films delivered a large discharge capacity compared with that of rGO papers or commercial diffusion layers (9760 mAh g⁻¹ at 100 mA g⁻¹).
These air cathodes were prepared by vacuum fil-
treatment was used to adjust the surface chemistry by re-
ducing the amount of oxygen and selectively removing partial-
ly unstable groups. With this simple methodology, a large dis-
charge capacity (19 800 mAh g\(^{-1}\)) over 50 cycles (1000 mA g\(^{-1}\)
to 1000 mA h g\(^{-1}\)) was achieved. Such enhancement was mainly attributed to the synergetic effect between the hierarchical structure and stable surface chemistry, which provided numerous reaction sites, strengthened reactant transfer, and reduced the formation of byproducts. The importance of the porous structure was also evaluated by Park et al., who studied the electrochemical performance of two types of commercial GNPs with different morphologies: sheetlike, with thin and wrinkled features, and granular, with disordered solid nanoparticles (NPs) of random aggregates.\(^{[28]}\) Graphene with wrinkled sheets presented a better electrochemical performance (3840 versus 255 mA h g\(^{-1}\)) and was stable for 40 cycles, due to a wider pore

Table 1. Summary of relevant materials reported in the literature for pure graphene-based cathodes in Li–O\(_2\) batteries.\(^{[24]}\)

| Material                      | Synthesis                        | Electrolyte                        | Discharge capacity (discharge rate) | Capacity limitation | Cycles (discharge rate) | Ref.     |
|-------------------------------|----------------------------------|------------------------------------|-------------------------------------|---------------------|-------------------------|----------|
| expanded rGO paper            | vacuum-promoted expansion        | 0.1 M LiClO\(_4\) in DMSO           | 18 900 mAh g\(^{-1}\) (300 mA g\(^{-1}\)) | 1000 mAh g\(^{-1}\) | 50                      | [27]     |
| GNPs                          | commercially available           | 1 M LiBF\(_4\) in NMP               | –                                   | 1000 mAh g\(^{-1}\) | 40                      | [28]     |
| rGO paper                     | Hummer’s method + chemical redu-
tion + freeze drying + thermal redu-
tion + hydrothermal carbonization of glucose on GO + KOH activation | 1 M LiN\(_3\)O in DMAc              | 497 mAh g\(^{-1}\) (0.1 mA cm\(^{-2}\)) | none                | 85                      | [25]     |
| 3D rGO membrane               | Hummer’s method + coating in CP  | 1 M LiN\(_3\)O in DMAc              | –                                   | 1425 mAh g\(^{-1}\) | 100                     | [29]     |
| 3D paperlike graphene         | templating with polystyrene parti-
cles with commercial GO + thermal redu-
tion + coating in CP + freeze drying + thermal redu-
tion + hydrothermal carbonization of glucose on GO + KOH activation | 1 M LiN\(_3\)O in DMAc              | –                                   | 1000 mAh g\(^{-1}\) | 78                      | [30]     |
| rGO/activated carbon          | hydrothermal carbonization of glu-
cose on GO + KOH activation       | 1 M LiCF\(_3\)SO\(_4\) in TEGDME     | 3.2 mAh cm\(^{-2}\) (0.05 mA cm\(^{-2}\)) | 0.1 mAh cm\(^{-2}\) | 170                     | [34]     |

[24] GNP = graphene nanoplatelet, rGO = reduced graphene oxide, CP = carbon paper, GO = graphene oxide, NMP = N-methyl-2-pyrrolidone, LiTFSI = lithium bis(trifluoromethanesulfonyl)imide, TEGDME = tetraethylene glycol dimethyl ether, DMAc = dimethylacetamide.
size distribution, which provided mesoporous channels for suitable electrolyte, oxygen, and Li²⁻ diffusion. The development of well-defined porous structures delivered the most promising results regarding pure graphene-based materials. Hence, Zhong et al. manufactured 3D rGO-based membranes by depositing a freeze-dried GO aerogel onto CP followed by annealing.[29] This work demonstrated that the molecular diffusion rate, O₂/H₂O selectivity, and moisture-resistant behavior could be tuned by controlling both the density and thickness of the graphene gel. The highly tortuous hydrophobic graphene membrane retards moisture diffusion and, thus, boosts cycling performance under ambient conditions. As observed in Figure 2, this material exhibited excellent cycling performance (>2000 cycles under a capacity limitation regime of 140 mAh g⁻¹ and >100 cycles under a cutoff of 1425 mAh g⁻¹) and high capacity (>5700 mAh g⁻¹ over 20 cycles at a high current density of 2.8 A g⁻¹).

The influence of larger pore size on performance was studied by the groups of Kim and Yu, who prepared 3D macroporous paperlike graphene by using polystyrene colloidal particles as a sacrificial template.[30, 31] More than 100 cycles were achieved at a current density of 500 mA g⁻¹ under a capacity limitation of 1000 mAh g⁻¹ due to the tailored macroporosity.

Three-dimensional graphene mesoporous foams also showed improved performance, as further demonstrated by the groups of Liu and Zhang.[32, 33] In the first case, the open network structure was obtained by directly growing graphene in aluminum current collectors, which allowed the coexistence of open cages and honeycomb channels that facilitated O₂ gas diffusion, while providing a large surface area for the deposition of discharge products.[32] In the second study, the electrochemical exfoliation of highly ordered pyrolytic graphite, followed by thermal reduction at different temperatures, resulted in graphene foam cathodes; the best electrochemical performance was attained at 800 °C.[33]

Another approach to enhance the cathode porosity includes coating of the graphene surface with porous carbon to provide numerous meso-/micropores that act as nucleation sites for the discharge products. Such carbon–carbon hybrids not only avoid graphene restacking, but also provide a large surface area and enhanced conductivity. In this regard, Xin et al. prepared graphene–hydrothermally activated carbon by using glucose and GO precursors, followed by chemical activation with KOH.[34] The hybrid nanostructure suppressed Li₂O₃ grain growth, leading to small particles, compared with 100–200 μm toroidal particles observed on pristine rGO. The benefits of hybridizing graphene-based materials with tailored carbons was demonstrated by a discharge capacity of 1800 μAh cm⁻² and an improved cyclability (170 stable cycles). Wang et al. also prepared graphene cathodes with hierarchical porosity through a facile and effective in situ sol–gel method, using resorcinol/formaldehyde cross-linkers as the carbon source and a nickel foam template.[35] The hybrid presented an improved performance relative to that of isolated phases, showing discharge capacities as high as 11 060 mAh g⁻¹ (280 mA g⁻¹).

The abovementioned studies show that both porosity and morphology of the air cathode are key to Li₂O₂ battery performance; an open meso-/macroporous channel structure facilitates the suitable interconnection of graphene sheets, while enhancing Li²⁻ and O₂ diffusion and the accommodation of discharge products. Control of the porosity can also have electrocatalyst-like behavior by increasing the exposure of active sites (defects on graphene sheets) and, consequently, reducing the charge overpotential.

2.2. Graphene–metal and graphene–metal oxide composites

The ORR and OER are considered to be kinetically limiting processes due to their sluggish kinetics. The limited catalytic activity of graphene has inspired researchers to develop active electrocatalysts that can compensate for efficiency loss of the cell. Noble metals, first-row d-block metals, and their corresponding oxides have been identified as potential OER catalysts. The use of graphene as a conductive support for metal-based NPs not

Figure 2. Galvanostatic cycling of freeze-dried rGO deposited onto CP under a capacity limitation of a) 2850, b) 5700, and c) 140 mAh g⁻¹; and the corresponding cycling profiles (d–f) at a current density of 2.8 A g⁻¹. Reproduced from Ref. [29] with permission. Copyright 2017, Springer Science.
only contributes to the stability of the catalysts, but also to charge transfer and mass transport. Moreover, the incorporation of metal-based NPs onto the graphene surface avoids re-stacking of the sheets, which boosts the outstanding properties of this 2D material. Metal catalysts supported on graphene have been, therefore, widely investigated, of which ruthenium is one of the most studied noble metals.

Jung et al. evaluated the influence of anchoring ruthenium-based NPs (metallic Ru or hydrated Ru) onto rGO on the cell performance.[56] The hydrated Ru phase presented a lower charge overpotential than that of the metallic phase and delivered 30 cycles (500 mA g\(^{-1}\) to 5000 mA h g\(^{-1}\)) due to a lower bonding energy that better catalyzed the decomposition of discharge products. In a later study, they compared the catalytic activity of Ru with that of Pd and Pt[57] by synthesizing rGO/metal NP composites through a one-pot modified polyl synthetic method. NPs loaded on rGO helped to suppress the re-stacking of rGO sheets and the graphene sheets facilitated both a smaller particle size and uniform distribution of the metal particles. The resulting cathode material presented a higher surface area, and hence, accessible active catalytic sites. Pd/rGO, Pt/rGO, and Ru/rGO composites demonstrated a positive effect towards catalyzing the OER, whereas pristine rGO showed the ability to catalyze the ORR. Specifically, the Ru/rGO composite presented the lowest charge overpotential (Figure 3a) and longer cycle life (30 vs. 15 cycles). The improved catalytic behavior of the Ru/rGO composite can be ascribed to the ability of Ru to induce morphological changes in the discharge products; a thin film of LiO\(_2\) formed instead of typical big toroids.

Wu et al. continued to study hydrated amorphous RuO\(_2\) (20–100 nm) supported on rGO (Table 2).[38] They confirmed the tailored morphology of the LiO\(_2\) discharge product due to the presence of Ru in the composite, which resulted in a pronounced reduction of the first cycle overpotential (Figure 3b) and an enhanced cycle life in comparison with that of previous studies (55 cycles). Similar performance was attained by Jiang et al., who used self-standing graphene-based aerogels decorated with Ru NPs, which were synthesized by means of a simple hydrothermal method.[59]

Despite of the reasonable performance of Ru-based catalysts, Pt has been considered as the reference metal catalyst for the ORR and OER due to its outstanding catalytic activity. Yang et al. prepared highly dispersed Pt NPs–GNS hybrids by liquid-phase pulsed laser ablation,[60] which delivered a discharge capacity of 4800 mA h g\(^{-1}\) and reduced considerably the first cycle overpotential. However, the high cost of platinum, together with self-poisoning issues derived from the strong ad-

Table 2. Summary of relevant materials reported in the literature for noble-metal-based catalysts anchored on graphene-based materials in Li–O\(_2\) batteries.\(^{(a)}\)[56]

| Metal catalyst | Material Synthesis | Electrolyte (in TEGDME) | Discharge capacity (discharge rate) | Capacity limitation | Cycles (discharge rate) | Ref. |
|----------------|-------------------|------------------------|-----------------------------------|-------------------|-------------------------|------|
| Ru             | hydrous amorphous RuO\(_2\)/rGO | Hummer’s method | 1 M LiTFSI | – | 1000 mA h g\(^{-1}\) | 55 | [38] |
| Pd             | Pd/GNS | – Ru incorporation by sol–gel method | simultaneous reduction of GO and Pd precursor | 1 M LiCF\(_2\)SO\(_3\) | 7680 mA h g\(^{-1}\) (0.08 mA cm\(^{-2}\)) | 500 mA h g\(^{-1}\) | 100 | [43] |
|                | graphene/Au NPs/ Au NS sandwich | – Au deposition by solution impregnation | | 1 M LiClO\(_4\) | 3347 mA h g\(^{-1}\) (400 mA g\(^{-1}\))\(^{(b)}\) | 500 mA h g\(^{-1}\) | 300 | [47] |
| Au             | Au/rGO | Hummer’s method | – simultaneous reduction of GO and Au precursor | 1 M LiPF\(_6\) | 5230 mA h g\(^{-1}\) (0.1 mA cm\(^{-2}\)) | none | 120 | [48] |
| Ir             | Ir/deoxygenated graphene | modified Hummer’s method | – Ir incorporation by ethylene glycol reduction | 0.1 M LiClO\(_4\)\(^{(c)}\) | – | 1000 mA h g\(^{-1}\) | 150 | [51] |

(a) CVD = chemical vapor deposition. (b) Capacity and current density calculated on the basis of catalyst only. (c) In TEGDME/DMSO.

Figure 3. a) Discharge–charge voltage curves of lithium-air batteries by using noble-metal catalysts supported on a rGO electrode. Reproduced from Ref.[37] with permission. Copyright 2015, American Chemical Society. b) Voltage profiles of Super P, rGO, and rGO/hydrous amorphous RuO\(_2\) composite. Reproduced from Ref.[38] with permission. Copyright 2016, Royal Society of Chemistry.
sorption of carbonaceous intermediates on the platinum surface, restricted its early commercialization.

In this sense, palladium has been studied as a potential replacement and has attracted considerable attention because of its high catalytic activity and relatively low cost. Ye et al. reported the preparation of alloyed PtPd NPs anchored on the surface of graphene. The poisoning resistance of palladium, combined with the high electroactivity of platinum, resulted in an enhanced electrochemical performance. An adequate ratio of Pt to Pd was established to be Pt$_{60}$Pd$_{40}$, which resulted in a lower first cycle overpotential and the best cyclability (80 cycles at 200 mA g$^{-1}$ to 1000 mA h g$^{-1}$) among different alloying ratios.

Ye et al. achieved one of the highest cyclability values ever reported among noble-metal-based catalysts by anchoring platinum NPs on the surface of graphene. Highly homogeneously dispersed Pd NPs were supported on rGO sheets (Figure 4a) through functionalization of GO with Pd precursor and subsequent reduction with ethylene glycol. This composite delivered a discharge capacity of 7690 mA h g$^{-1}$ (at 80 μA h cm$^{-2}$) and almost 100 stable charge/discharge cycles. They also observed that palladium NPs had the ability to change the morphology of the discharge products to homogeneously distributed NPs (Figure 4b–g), which were easier to decompose during charging.

Ye et al. followed a different approach by using metallic Pd nanodendrites supported on graphene NPs. A discharge capacity of 3000 mA h g$^{-1}$ and stability for 30 cycles were obtained (200 mA g$^{-1}$), with a considerable reduction in the charge/discharge overpotential, in comparison with that of bare graphene electrodes. The branched structure of nanodendrites improved the electrochemical activity, due to the higher surface area and location of catalytically active sites at the corners, edges, and stepped atoms along their branches.

Despite the positive performance of Pd and Pt metals, their high cost requires an investigation of new approaches. The use of much cheaper 3d transition metals arose as an economically feasible alternative for the possible mass production of future Li–O$_2$ batteries. In this sense, Sevim et al. reported two different studies to alloy Pd$^{43}$ and Pt$^{46}$ with Co, Ni, and Cu. These NPs were synthesized through the chemical reduction of metal precursors, which were further dispersed in rGO sheets by liquid self-assembly. Regarding Pd alloys, the NiPd-based cathode delivered the best performance in terms of cyclability. For Pt alloys, PtCo showed 80 cycles (0.15 mA cm$^{-2}$ to 0.75 mA h cm$^{-2}$), whereas PtNi and PtCu were more resistant to carbon corrosion. In accordance with previous studies, the use of different Pt alloys induces morphological changes in the discharge products, and hence, influences the subsequent recharge process.

Gold has also been explored as a bifunctional catalyst in several studies in the field of Li–O$_2$ cathodes. Thus, a complex synthetic approach was presented by Wane et al.$^{47}$ in which Au NPs were sandwiched between Au nanosheets (NS) and GNSs

![Figure 4. a) Schematic illustration of a Pd-functionalized GNS cathode catalyst for a Li–O$_2$ battery. PDDA = poly(diallyldimethylammonium chloride). SEM images evaluating the evolution of the discharge products for pristine GNSs (b–d) and Pd/GNS (e–g). Reproduced from Ref. [43] with permission. Copyright 2015, Royal Society of Chemistry.](image-url)
(Figure 5a). The resulting material showed a discharge capacity of 3347 mAh g\textsuperscript{-1} and was stable for 170 and 300 cycles (400 mA g\textsuperscript{-1}) under a capacity limitation regime of 500 and 1000 mAh g\textsuperscript{-1}, respectively (Figure 5b and c). These excellent results could be ascribed to the design of the electrode, which delayed deactivation of the electrode and reduced contact of Li\textsubscript{2}O\textsubscript{2} with both graphene and electrolyte.

Kumar et al. reported a simpler synthetic method based on the anchoring of Au NPs on rGO by simultaneous reduction of Au\textsuperscript{3+} and GO in water with NaBH\textsubscript{4}.\textsuperscript{[46]} This method was also followed in two subsequent studies to evaluate the performance of Ag\textsuperscript{[49]} and Ir\textsuperscript{[50]} NPs anchored onto rGO sheets. In the case of Au NPs, the first cycle overpotential was considerably reduced and 120 cycles were obtained without a capacity limitation regime. In the case of Ag NPs, even if a higher discharge capacity was retained (11.29 mAh cm\textsuperscript{-2} at 0.2 mA cm\textsuperscript{-2}), cyclability was limited to only 30 cycles. In addition, a lower coulombic efficiency was obtained compared with that of Au NPs. Finally, the Ir/rGO composite displayed a high discharge capacity (11.36 mAh cm\textsuperscript{-2}) and retained a good coulombic efficiency during cycling.

The incorporation of Ir NPs into deoxygenated 3D porous graphene frameworks was explored by Zhou et al. through vacuum-promoted exfoliation and heat treatment.\textsuperscript{[51]} Iridium was incorporated by means of a wet reduction method, leading to iridium NPs uniformly dispersed on the graphene surface. This composite showed excellent cyclability for 150 cycles (2000 mA g\textsuperscript{-1} to 1000 mAh g\textsuperscript{-1}). The hierarchical framework provided unimpeded transport of oxygen, exposed catalytic sites, and stable surface for the electrochemical reaction, while Ir NPs increased the electrocatalytic activity towards the formation/decomposition of Li\textsubscript{2}O\textsubscript{2}.

Despite the great catalytic activity of noble metals, their scarcity and high cost have tremendously limited their practical feasibility. The exploration of earth-abundant-element catalysts without compromising the catalytic performance is still a big challenge, for which research has focused on developing non-noble-metal and metal oxide catalysts.\textsuperscript{[52]} Cobalt is the most explored element due to the good performance demonstrated in other technologies, such as Li\textsubscript{2}S; however, its use is still restrained by its low conductivity and low surface area. Different strategies have been investigated to overcome these drawbacks, such as controlling the morphology of Co NPs or adding conductive graphene-based materials as a matrix to alleviate the insulating nature of cobalt oxides (Table 3).\textsuperscript{[53]}

Ryu et al. proposed a GNF/1D Co\textsubscript{3}O\textsubscript{4} nanofiber composite bi-functional cathode.\textsuperscript{[54]} Co\textsubscript{3}O\textsubscript{4} nanofibers were prepared by electrospinning and, subsequently, dispersed in a suspension of GNFs. A discharge capacity of 10500 mAh g\textsuperscript{-1}, a high coulombic efficiency in the first cycle (>90%), and stability over 80 cycles (1000 mAh g\textsuperscript{-1} at 200 mA g\textsuperscript{-1}) were achieved. The large surface to volume ratio of this 1D nanostructure facilitated a continuous, one-way, electron-transport pathway with numerous reaction sites. Yuan et al. compared the performance of CoO nanocrystals\textsuperscript{[55]} with that of Co\textsubscript{3}O\textsubscript{4} nanorods\textsuperscript{[56]} CoO nanocrystals were obtained by simply dispersing a CoO precursor in GO sheets and heating, whereas Co\textsubscript{3}O\textsubscript{4} nanorods were attained through a hydrothermal synthesis followed by thermal treatment. A considerable decrease in the first cycle overpotential was observed, which indicated efficient catalytic activity of cobalt oxides towards the ORR/OER, of which the OER process was particularly favored. It is also notable that the overpotential was lower if cobalt oxides were anchored on graphene-based materials, due to an increase in conductivity and a better dispersion of NPs within the matrix. Even if the discharge capacity of CoO nanocrystals was higher than that of Co\textsubscript{3}O\textsubscript{4} nanorods (14450 vs. 7600 mAh g\textsuperscript{-1}), the latter showed an improved cycling performance (42 cycles with a capacity limitation of 1500 mAh g\textsuperscript{-1}). Co\textsubscript{3}O\textsubscript{4} NSs were also investigated by Song et al., who used a simple hydrothermal synthesis.\textsuperscript{[56]} The authors claimed that graphene not only contributed to the uniform dispersion of the NS catalyst, which provided more active sites for the ORR and OER, but also to the accommodation of insoluble discharge products due to the high surface area available. The discharge capacity of the bare catalyst was considerably improved by the presence of the rGO matrix (10528 vs. 4841 mAh g\textsuperscript{-1} at 100 mA g\textsuperscript{-1}). Moreover, the first cycle charge overpotential and cyclability were improved by the utilization of this composite, for which stability over 113 and 28 cycles were attained (1000 and 3000 mAh g\textsuperscript{-1}, respectively). It is worth noting that the carbon content in the electrode was only 6 wt %, which reduced parasitic reactions and poisoning of the catalyst, and thus, enhanced the cycling life.

Figure 5. a) Schematic illustration of the GNS/Au NP/Au NS electrode on Ni and its working mechanism. Corresponding cycling performance under a capacity limitation regime of b) 500 and c) 1000 mA g\textsuperscript{-1}. Reproduced from Ref. [47] with permission. Copyright 2016, Wiley-VCH.
Table 3. Summary of relevant materials reported in the literature for transition-metal-based catalysts anchored on graphene-based materials for Li–O₂ batteries.

| Metal catalyst | Material | Synthesis<sup>[a]</sup> | Electrolyte | Discharge capacity<sup>[discharge rate]</sup> | Capacity limitation<sup>[discharge rate]</sup> | Cycles<sup>[discharge rate]</sup> | Ref. |
|----------------|----------|---------------------------|-------------|---------------------------------------------|---------------------------------------------|---------------------------------|-----|
| Co             | Co₃O₄ nanofibers/graphene | Co₃O₄ preparation by electrospinning + mixing with GNF suspension and drying | 1M LiTFSI in TEGDME | 10,500 mAh g<sup>-1</sup> (200 mA g<sup>-1</sup>) | 1000 mAh g<sup>-1</sup> (100 mA g<sup>-1</sup>)<sup>[b]</sup> | 80 (200 mA g<sup>-1</sup>) | [54] |
| Co₃O₄ NS/graphene NS | modified Hummer’s method + simultaneous hydrothermal reduction of GO and Co₃O₄ precursor | – | 10,528 mAh g<sup>-1</sup> (100 mA g<sup>-1</sup>)<sup>[b]</sup> | 1000 mAh g<sup>-1</sup> | 113 (100 mA g<sup>-1</sup>)<sup>[b]</sup> | [56] |
| CoCu yolk–shell/graphene | modified Hummer’s method + simultaneous hydrothermal reduction of GO and CoCu precursor | 1M LiTFSI in TEGDME | 15,000 mAh g<sup>-1</sup> (200 mA g<sup>-1</sup>) | 1000 mAh g<sup>-1</sup> | 204 (200 mA g<sup>-1</sup>) | [57] |
| Cu             | CuO NW/graphene | simultaneous chemical reduction of graphene and CuO NW precursor | 1M LiNO₃ in DMAc | – | 1000 mAh g<sup>-1</sup> | 120 (1000 mA g<sup>-1</sup>) | [59] |
| Ni             | NiO nanoplatelets/graphene | modified Hummer’s method followed by thermal treatment to produce GNS + simultaneous hydrothermal reduction of GNS and NiO precursor | 1M LiTFSI in TEGDME | 2400 mAh g<sup>-1</sup> (500 mA g<sup>-1</sup>) | none | 60 (400 mA g<sup>-1</sup>)<sup>[b]</sup> | [67] |
| Mn             | flowerlike α-MnO₂/graphene | graphene deposition on Ni foam by CVD + deposition of MnO₂ on 3D graphene/Ni by hydrothermal treatment | 0.1 M LiClO₄ in DME | 5230 mAh g<sup>-1</sup> (0.083 mACm<sup>-2</sup>)<sup>[c]</sup> | 492 mAh g<sup>-1</sup> | 132 (0.33 mACm<sup>-2</sup>)<sup>[c]</sup> | [64] |
| α-MnO<sub>2</sub>/graphene | modified Hummer’s method + microwave irradiation to GO + simultaneous microwave reduction of graphene and KMnO₄ | 1M LiClO₄SO₃ in TEGDME | 5862 mAh g<sup>-1</sup> (1000 mA g<sup>-1</sup>) | 1000 mAh g<sup>-1</sup> | 50 (100 mA g<sup>-1</sup>)<sup>[c]</sup> | [63] |
| Ce             | Ce₆Gd₄O₁₉/rGO | modified Hummer’s method + simultaneous hydrothermal reduction of GO and Gd/Ce precursors | 1M LiTFSI in DMSO | 15,069 mAh g<sup>-1</sup> (300 mA g<sup>-1</sup>) | 600 mAh g<sup>-1</sup> | 110 (400 mA g<sup>-1</sup>)<sup>[c]</sup> | [70] |
| spinels       | MnCOO<sub>2</sub> nanospheres/rGO | simultaneous sonochemical reduction of graphene and MnCOO<sub>2</sub>precursors | 1M LiTFSI in TEGDME | – | 1000 mAh g<sup>-1</sup> | 250 (800 mA g<sup>-1</sup>)<sup>[c]</sup> | [73] |
| NiCoO<sub>2</sub> needlelike/rGO foam | modified Hummer’s method + incorporation of NiCoO<sub>2</sub> by simultaneous hydrothermal treatment of NiCoO<sub>2</sub> precursors in the presence of graphene | 1M LiTFSI in DMSO | 6000 mAh g<sup>-1</sup> (300 mA g<sup>-1</sup>) | 1000 mAh g<sup>-1</sup> | 110 (400 mA g<sup>-1</sup>)<sup>[c]</sup> | [74] |
| CuCr<sub>2</sub>O₄ needlelike/rGO foam | hydrothermal treatment to synthesize CuCr<sub>2</sub>O₄ + simultaneous reduction of GO and CuCr<sub>2</sub>O₄ | 1M LiTFSI in TEGDME | – | 1000 mAh g<sup>-1</sup> | 100 (200 mA g<sup>-1</sup>) | [75] |

<sup>[a]</sup> GNF = graphene nanoflake. <sup>[b]</sup> Capacity and current density calculated on the basis of catalyst only. <sup>[c]</sup> Capacity and current density calculated on the basis of the composite (graphene + catalyst).
As an alternative to oxide-based catalysts, cobalt alloyed with other metals has also been explored. Chen et al. prepared copper particles covered by a cobalt shell supported on graphene through a simple hydrothermal method (Figure 6a). The synergistic effects of Co, Cu, and graphene in the final bimetallic composite are observed in Figure 6b; a high discharge capacity (15 000 mAh g⁻¹ at 200 mA g⁻¹) and good cyclability (Figure 6c) were achieved (122 and 204 cycles at a cutoff voltage of 2.5 and 2 V, respectively; 1000 mAh g⁻¹ at 200 mA g⁻¹).

The group of Wang et al. reported the preparation of 2D nanocomposites by anchoring an Al/Co hybrid layered double hydroxide onto rGO. The presence of graphene sheets in the nanocomposite reduced the charge/discharge overpotential by minimizing hydroxide particle agglomeration, while providing sufficient pathways for oxygen/electrolyte/electron transport and enough space for the deposition of the discharge products. The Li₂O₂ particles nucleated uniformly around the layer oxide sheets, and thus, prevented overgrowth of the discharge product and subsequently favored the recharging process.

Copper metal oxide in the shape of nanoleaves and nanowires was also explored by anchoring CuOH into graphene sheets with final reduction to CuO at low temperature. The presence of the catalyst allowed the reduction of the overpotential from 1.58 to 1.39 V and was stable over 120 cycles (1000 mAh g⁻¹ at 1000 mA g⁻¹).

The use of manganese oxides has emerged due to a favorable compromise between electrocatalytic activity, cost, ease of preparation, and environmentally friendliness. Débart and co-workers systematically studied the catalytic performance of Mn₃O₄, Mn₅O₃, and MnO₂ (α, β, γ, and λ phases). Among them, the α-MnO₂ catalyst exhibited excellent round-trip efficiency, a high specific capacity, and good cycling stability.

Numerous studies have reported the hybridization of MnO₂ with graphene due to the poor conductivity of this oxide; graphene acts as a conducting agent without compromising the effectiveness of the catalysts. For instance, Cao et al. studied the performance of α-MnO₂ anchored on rGO with 80 or 92 wt% of the transition-metal oxide catalyst. Composites of α-MnO₂/rGO, yielding different morphologies of the metal oxide (nanorods, nanowires, and mixtures), were obtained by the spontaneous redox reaction of rGO and KMnO₄. The morphology of the catalyst was a key point in the electrochemical performance of the hybrids, since the mixture of nanowires and nanorods delivered the lowest first cycle overpotential and highest discharge capacity. A low fraction of graphene in the composite led to a considerable reduction in parasitic reactions and longer cycle life. α-MnO₂ nanowires/rGO composites were obtained by the spontaneous redox reaction of rGO and KMnO₄. The morphology of the catalyst was a key point in the electrochemical performance of the hybrids, since the mixture of nanowires and nanorods delivered the lowest first cycle overpotential and highest discharge capacity. A low fraction of graphene in the composite led to a considerable reduction in parasitic reactions and longer cycle life. α-MnO₂ nanowires/rGO composites were obtained by the spontaneous redox reaction of rGO and KMnO₄. The morphology of the catalyst was a key point in the electrochemical performance of the hybrids, since the mixture of nanowires and nanorods delivered the lowest first cycle overpotential and highest discharge capacity. A low fraction of graphene in the composite led to a considerable reduction in parasitic reactions and longer cycle life. α-MnO₂ nanowires/rGO composites were obtained by the spontaneous redox reaction of rGO and KMnO₄. The morphology of the catalyst was a key point in the electrochemical performance of the hybrids, since the mixture of nanowires and nanorods delivered the lowest first cycle overpotential and highest discharge capacity. A low fraction of graphene in the composite led to a considerable reduction in parasitic reactions and longer cycle life. α-MnO₂ nanowires/rGO composites were obtained by the spontaneous redox reaction of rGO and KMnO₄. The morphology of the catalyst was a key point in the electrochemical performance of the hybrids, since the mixture of nanowires and nanorods delivered the lowest first cycle overpotential and highest discharge capacity. A low fraction of graphene in the composite led to a considerable reduction in parasitic reactions and longer cycle life.

Although α-MnO₂ is the most studied allotrope (due to its accessibility and easy preparation), other structures have also been investigated. In this regard, Yang et al. anchored γ-MnO₂ clusters onto rGO through pyrrole-assisted synthesis, through which a high discharge capacity of 11 235 mAh g⁻¹ (75 mAh g⁻¹) was attained and stability over 30 cycles was delivered. The combination of δ-MnO₂ (birnessite-type manga-
nane oxide) with graphene demonstrated the best performance in terms of cyclability. In this regard, Wang et al. prepared $\delta$-MnO$_2$ by an in situ, fast, and environmentally friendly microwave route.$^{[64]}$ Discharge capacities of 5862 and 3566 mAh g$^{-1}$ were delivered at 100 and 600 mA g$^{-1}$, respectively, and stability over 50 cycles was attained (100 mA g$^{-1}$ to 1000 mA g$^{-1}$). However, among all reported studies, the best results were obtained by Liu et al., who used a binder-free air electrode composed of 3D graphene deposited onto Ni foam with flowerlike $\delta$-MnO$_2$. $^{[64]}$ Graphene was deposited onto 3D Ni foam by means of CVD for the subsequent growth of ultrathin NSs of flowerlike $\delta$-MnO$_2$ through a facile hydrothermal route. The presence of $\delta$-MnO$_2$ decreased the charge overpotential compared with that of pure graphene (4.2 vs. 4.5 V) and increased the discharge plateau up to 2.8 V. Stability over 130 cycles was obtained (0.333 mA cm$^{-2}$ to 492 mAh g$^{-1}$), which could be ascribed to the efficient deposition of graphene on the skeleton of the Ni foam, and thus, favoring oxygen and electron pathways without blocking the pores. The flowerlike NS morphology in $\delta$-MnO$_2$ supplies a large number of efficient catalytic sites and, at the same time, provides enough space to accommodate the insoluble discharge products generated during cycling.

Li et al. prepared well-distributed particles of Mn$_3$O$_4$ catalyst over the surface of graphene sheets by reduction of manganese acetate in the presence of rGO.$^{[65]}$ Mn$_3$O$_4$/rGO composite was able to deliver a discharge capacity of 16200 mAh g$^{-1}$ (50 mA g$^{-1}$), but only 20 stable cycles were obtained under a regime without capacity limitation at the same current density.

Other earth-abundant elements with reduced cost and high efficiency, such as Fe, Ni, Ce, Gd, and Zr, have also been investigated as potential replacements for noble-metal catalysts. Zhang et al. proposed an interesting approach in which Fe$_2$O$_3$ nanocluster-decorated graphene composites were obtained by simultaneous electrochemical exfoliation.$^{[66]}$ This composite delivered a discharge capacity of 8290 mAh g$^{-1}$ (100 mA g$^{-1}$); however, only 30 cycles were achieved (200 mA g$^{-1}$ to 1000 mA g$^{-1}$).

Qiu et al. explored the performance of Ni metal by the in situ growth of NiO nanoplatelets on GNS through the thermal decomposition of Ni(OH)$_2$. $^{[67]}$ This cathode delivered a discharge capacity of 2400 mAh g$^{-1}$ and 60 cycles (50 mA g$^{-1}$) under a regime without capacity limitation, with a specific capacity of about 1200 mAh g$^{-1}$ in the 60th cycle. An additional study on Ni was performed by Zhu et al., who reported the preparation of a composite consisting of NiO/Ni--graphene foam by a simple hydrothermal method and subsequent thermal treatment.$^{[68]}$ The homogeneous distribution of NiO particles provided a discharge capacity of 25986 mAh g$^{-1}$ (100 mA g$^{-1}$) such as a high discharge capacity was ascribed to the ability of NiO particles to lower the reaction barrier, together with the 3D network structure of the graphene foam, which exposed more active sites and speeded up electron transfer.

Ceria (CeO$_2$) has also arisen as an attractive catalyst due to its high redox activity and ability to enhance the reactivity of other elements. Cerium-doped with rare-earth elements has demonstrated to have a tremendous effect on increasing the kinetics of the ORR and OER. Hence, the catalytic activity of Zr- and Gd-doped ceria NPs was explored by the groups of Ahn$^{[69]}$ and Jiang, $^{[70]}$ respectively. Zirconium-doped cathodes had a more pronounced effect on the ORR, whereas gadolinium had a major effect on the OER. Regarding cycling stability, only 14 cycles were achieved for Zr-based catalysts (1 mA cm$^{-2}$ to 500 mAh g$^{-1}$), whereas Gd proved to be more effective by delivering 110 stable cycles (400 mA g$^{-1}$ to 600 mAh g$^{-1}$). The uniform dispersion of CeO$_2$/Gd particles on the rGO surface promoted the deposition of Li$_2$O$_2$ nuclei and Gd$^{3+}$ stabilized CeO$_2$ NPs; thus, the overpotential gap is reduced to 0.89 V.

In the last five years, numerous research studies have been devoted to the use of double-metal oxides (specifically spinel ternary oxides). Cao et al. reported the preparation of CoFe$_2$O$_4$/rGO composites by a simple hydrothermal method.$^{[71]}$ The resulting composite delivered a discharge specific capacity of 2116 mAh g$^{-1}$ at a relatively low current density (50 mA g$^{-1}$). The authors observed that the presence of CoFe$_2$O$_4$ led to a considerable reduction of the first cycle overpotential and an improvement in the coulombic efficiency, delivering 30 cycles under a capacity limitation regime of 173 mAh g$^{-1}$ at 50 mA g$^{-1}$.

Among different spinel-based materials, XCo$_3$O$_4$-based (X = Zn, Ni, Mn, etc.) structures have been widely investigated, thanks to their ability to enhance the kinetics of the ORR and OER. Kim et al. developed nanowire-shaped MnCo$_2$O$_4$ anchored on rGO sheets to increase the spinel conductivity.$^{[72]}$ The 1D catalyst was obtained from the pyrolysis of MnCo$_2$(C$_2$O$_4$)$_3$ nanowires and subsequently mixed with rGO to achieve the final composite. Despite the designed nanowire morphology, only 35 cycles and a discharge capacity of 2218.4 mAh g$^{-1}$ at a relatively low current density (50 mA g$^{-1}$) were achieved. In contrast to this poor result, Karkera et al. reported one of the highest performances regarding metal-based electrocatalysts by using MnCo$_2$O$_4$ nanospheres.$^{[73]}$ This advanced air cathode was prepared by dispersing both manganese and cobalt acetate in a basic suspension of graphene and applying ultrasound frequencies to promote the formation and grafting of the spinel into the graphene support (Figure 7a). The resulting composite delivered 250 stable cycles under a capacity limitation regime of 1000 mAh g$^{-1}$ at a relatively high current density (800 mA g$^{-1}$). It is worth noting that this performance is really close to that of Au NPs$^{[47]}$ and the graphene content in the composite is only 5 wt%. The porous channels in MnCo$_2$O$_4$ nanospheres facilitated oxygen intake into the bulk material along the graphene surface, which allowed a larger exposure of active sites for the ORR and OER; thus, the cyclability was improved due to slower saturation of the cathode surface. The cyclability values achieved by Jiang et al. with Ni metal as a substitute element into the spinel lattice were also close to those reported for noble metals.$^{[74]}$ A needlelike NiCo$_2$O$_4$/rGO self-standing composite was obtained following the synthetic procedure represented in Figure 7b.

The cathode delivered a discharge capacity of 6000 mAh g$^{-1}$ (300 mA g$^{-1}$) and was stable for more than 100 cycles under a capacity limitation regime of 1000 mAh g$^{-1}$ (400 mA g$^{-1}$). The high catalytic activity of the spinel was confirmed by the re-
duction of the first cycle overpotential compared with that of pure graphene material and it resulted from the formation of a film-like discharge product.

Similar cyclability results were obtained by Liu et al., who proposed the use of CuCr₂O₄ needlelike NPs anchored onto the surface of rGO. The composite was obtained by a simple hydrothermal method of the spinel precursor in the presence of GO (10 wt%) followed by thermal treatment. The authors claimed that the use of rGO as a conductive support provided a suitable distribution/connection of Cu-substituted spinel NPs, which led to increased electronic conductivity, provided pathways for Li⁺ transport, and buffered volume changes during cycling. The composite was stable for 100 cycles under a capacity limitation regime of 1000 mAh g⁻¹ (200 mA g⁻¹).

2.3. Heteroatom-doped or functionalized graphene

Metal-free graphene catalysts have been explored as promising alternatives to the use of precious metals. Doping graphene with heteroatoms, such as nitrogen, sulfur, or oxygen, alters the physicochemical properties of the materials and creates structural defects, which favor the ORR/OER activity (Table 4).

Li and co-workers studied the catalytic behavior of nitrogen-doped (N-GNSs) and sulfur-doped (S-GNSs) in comparison to that of pristine GNS, for the first time. N-GNS presented a higher average discharge plateau and an increase of about 40% in the discharge capacity (11 660 mAh g⁻¹ at 75 mA g⁻¹), whereas S-GNS presented improved behavior during charging. The discharge product morphology was greatly influenced by chemical doping; aggregated particles were observed on GNS cathodes (Figure 8a), highly distributed particles were observed on N-GNSs (Figure 8b), and large nanorods grew on the surface of S-GNSs (Figure 8c). The authors stated that the strong interaction between the intermediate products and pyridinic/quaternary nitrogen groups on the surface of the graphene promoted the nucleation of Li₂O₂ particles, while thiophene/thioether-like functionalities promoted better charging behavior.

The influence of N and S doping was also studied by Bae et al., who reported that S-doped electrodes presented a high proportion of sulfonates. The discharge capacity of the doped cathodes was clearly enhanced and the S-doped cathode delivered the best performance (1980 mAh g⁻¹ at 0.1 mA cm⁻²). The enhanced ORR catalytic behavior of both N- and S-doped electrodes was attributed to additional defect sites that promoted nucleation of the discharge products. The obtained results suggested that inorganic sulfonates and pyridinic groups catalyzed the ORR, whereas organic C–S–C-like functionalities facilitated the OER. The effect of oxygen atoms on the electrocatalytic performance of graphene-derived air electrodes was reported by the group of Storm, who varied the oxidation time of graphite to obtain GO sheets oxidized to different extents and reduced them either with hydrazine or by thermal treatment. The use of highly oxidized GO precursor and thermal reduction resulted in the best electrochemical performance. This cathode yielded the highest proportion of carboxyl, carboxyl, and lactol functionalities, as well as the highest structural order, with a specific capacity of 59792 mAh g⁻¹. Samples reduced with hydrazine, however, yielded the highest proportion of carboxyl/carboxyl species, while providing the best cycling behavior and lowest charging voltage. The presence of polar C=O bonds served as Li₂O₂ nucleation sites and introduced an increased oxide coverage of the cathode. The impact of chemical doping on the structural order (i.e., creation of defects) of graphene-derived materials was investigated by Shui et al. and further correlated with the performance in LiO₂ batteries. A highly defective graphene (Figure 8d) was prepared by the oxidation of commercial graphene powder and further thermal treatment. Both the rGO defective sheets and GO were doped with nitrogen to study the impact of nitrogen atoms on their structures. The impor-
The N-doped sample presented a well-defined surface (Figure 9f). The monitoring of the surface chemistry by means of X-ray photoelectron spectroscopy (XPS) revealed that the C–S–C species degraded gradually, while inactive sulfates remained after 300 cycles. Hence, organic C–S–C-like species were definitively identified as active species for the OER. He and co-workers also prepared 3D N-doped graphene through a facile hydrothermal process and subsequent freeze-drying/annealing of the resulting aerogel. The N-doped sample presented a well-defined meso-/macroporous structure with surface graphitic, pyrrolic, and pyridinic functionalities. The N-doped graphene not only exhibited the lowest charge overpotential among the three studied samples but was also capable of delivering a specific capacity of 10 400 mAh g\(^{-1}\) at 200 mA g\(^{-1}\) (Figure 9e) for N-doped graphene, as a consequence of surface chemistry rich in graphitic and pyridinic-like groups.

Sulfur-doped graphene not only exhibited the lowest charge overpotential among the three studied samples but was also capable of delivering a specific capacity of 10 400 mAh g\(^{-1}\) at 200 mA g\(^{-1}\) (Figure 9e) for N-doped graphene, as a consequence of surface chemistry rich in graphitic and pyridinic-like groups.

Several groups have also investigated the synergistic effect between the catalytic activity of heteroatoms and mass transport provided by porous structures. Three-dimensional N-doped interconnected graphene nanocages (Figure 9a) were prepared by Zhao et al. by using polydopamine/polystyrene sphere templates and hydrothermal/freeze-drying self-assembly of GO sheets.[81] The electrode, annealed at 1000 °C, delivered a specific capacity of 10 081 mAh g\(^{-1}\) at 200 mA g\(^{-1}\) (Figure 9b) and 72 cycles at a high current density of 300 mA g\(^{-1}\) with no capacity loss (Figure 9c). The enhanced kinetics were ascribed to 1) the presence of meso-/macropores, which are beneficial to the rapid transport of O\(_2\) and Li\(^+\); 2) the high specific area, which contributes to the triphase (solid–liquid–gas) regions; and 3) full exposure of the pyridinic nitrogen active sites.

Han et al. prepared 3D undoped and N- and S-doped nanostructured graphene by means of CVD (Figure 9d).[82] The capacity delivered by undoped and S-doped electrodes was very similar, about 4700 mAh g\(^{-1}\), but the capacity was as high as 10 400 mAh g\(^{-1}\) (Figure 9e) for N-doped graphene, as a consequence of surface chemistry rich in graphitic and pyridinic-like groups.

| Material | Synthesis | Electrolyte | Discharge capacity (mAh g\(^{-1}\)) | Capacity limitation | Cycles (discharge rate) | Ref. |
|----------|-----------|-------------|----------------------------------|-------------------|------------------------|------|
| N-doped defective GNSs | annealing of commercial Vor-X in an open furnace, reduction in NH\(_3\) or H\(_2\) at high temperature | 1M LiCF\(_3\)SO\(_3\) in TEGDME | 74 000 mAh g\(^{-1}\), 17 000 mAh g\(^{-1}\), 10 081 mAh g\(^{-1}\) | 880 mAh g\(^{-1}\) | 100 mA g\(^{-1}\) | [80] |
| S-GNSs | hydrothermal treatment of thiourea and GO as precursors and freeze-drying/annealing | 1M LiTFSI in TEGDME | 1 000 mAh g\(^{-1}\) | 100 mAh g\(^{-1}\) | 1000 mAh g\(^{-1}\), 200 mA g\(^{-1}\) | [82] |
| N-,S-codoped porous carbon/graphene hybrid | hydrothermal treatment of thiourea and sucrose+ KOH activation | 0.5M LiTFSI/0.5 LiNO\(_3\) in TEGDME | 11 491 mAh g\(^{-1}\) | 500 mAh g\(^{-1}\) | 1000 mAh g\(^{-1}\) | [84] |
| PEDOT microflower/GNS composites | surfactant-assisted polymerization | | 1500 mAh g\(^{-1}\) | 1500 mAh g\(^{-1}\) | 500 mAh g\(^{-1}\) | [86] |
Figure 8. SEM images of a) pristine GNS, b) N-GNS, and c) S-GNS. Reproduced from refs. [76, 77] with permission. Copyright 2012, Elsevier and Royal Society of Chemistry. d) TEM image of the defective GNS and e) a comparison of the discharge/charge curves of defective and nondefective N-GNS. Reproduced from Ref. [80] with permission. Copyright 2016, American Chemical Society.

Figure 9. SEM image of a) N-doped graphene nanocages (N-doped graphene aerogel (NPGA)); b) initial discharge/charge curves; and c) discharge capacity/discharge voltage as a function of the number of cycles for the N-doped graphene nanocages, unstructured graphene (graphene aerogel (GA)), and Super P. Reproduced from Ref. [81] with permission. Copyright 2015, Wiley-VCH. SEM image of d) 3D nanoporous electrode prepared by CVD; e) initial discharge/charge curves for pristine GNSs, N-GNSs, and S-GNSs; and f) cycling performance of 3D S-doped cathode. Reproduced from Ref. [82] with permission. Copyright 2016, Wiley-VCH.
The manufacture of graphene/conductive polymer composites is also a versatile alternative to tailor the chemistry of graphene-based electrodes. Hence, Selvaraj et al. grew polypyrrole (PPy) on the surface of rGO sheets;[85] the discharge capacity of the composite was considerably improved compared with that of pristine rGO (3358 vs. 911 mAh cm\(^{-2}\) at 0.3 mA cm\(^{-2}\)), as well as the charge overpotential (1.06 vs. 1.41 V). The cycling stability of the composite material was tested by subjecting the cell to 25 discharge–charge cycles at 0.5 mA cm\(^{-2}\) to about 2500 mAh g\(^{-1}\). Yoon and Park covered the surface of commercial graphene with PEDOT microflowers by controlled polymerization of the ether-/thiophene-containing polymer on a graphene suspension; however, this material showed insufficient capacity due to the low conductivity of the polymer.[86] To increase the conductivity of PEDOT microflowers, different proportions of graphene (5–20 wt %) were added to the polymer. The composite yielding 5 wt % graphene delivered the lowest overpotential and the best cycling performance by retaining 150 cycles with a constant capacity. It was proposed that redox-active conducting polymers presented a high catalytic activity for the formation–dissociation of Li\(_2\)O\(_2\), while suppressing side reactions triggered by high-surface-area carbon materials, such as graphene.

The catalytic performance of heteroatom-doped graphene is summarized in Figure 10. The functional groups that induce positive charge density on the carbon backbone enhance the adsorption of O\(_2\) molecules onto the graphene surface. The proximity between the O\(_2\) molecules and electrons delocalized throughout the \(\pi\)-conjugated system of graphene increases charge transfer to reduce O\(_2\) to O\(_2^\cdot\). Hence, pyridinic-like functionalities induce polarization in adjacent carbon atoms because nitrogen presents higher electronegativity than that of carbon.

On the other hand, quaternary nitrogen generates positive charges in the \(\pi\)-conjugated system; nitrogen bears one electron less in the valence band than carbon and can easily accommodate in the lattice due to a similar atomic size. Regarding oxygen and sulfur, their atomic size is larger than that of carbon, but they can be incorporated as functional groups at the edge of the carbon network. These terminal groups can either induce positive charge by resonance or favor the formation of defects by bending the planar structure of the carbon structure, which also enhances the catalytic performance of graphene. Finally, conducting polymers, such as PPy and PEDOT, also present a positive charge when oxidized to the bipolaron state, which favors the adsorption of O\(_2\) molecules and subsequent ORR during charging. On the contrary, aromatic sulfur groups (such as thiophene and thioethers) present \(\pi\) orbitals with polarizable electron pairs, which can decrease the bonding of O\(_2^\cdot\) species to the cathode surface, leading to a low passivation of the cathode throughout charging.

2.4. Multifunctional O\(_2\) electrode: Combining catalysts and heteroatoms in graphene nanostructures

In the previous sections, efforts to combine graphene with metal-based catalysts or heteroatoms have been analyzed. In this section, both strategies are combined to develop bifunctional air cathodes able to surpass the limitations mentioned in previous sections (Table 5). Wu et al. designed a composite consisting of a 3D hollow network support built from graphene nanocages, in which they deposited homogenously ul-

![Figure 10. Mechanisms affecting the catalytic performance of heteroatom-doped graphene compared with that of undoped graphene.](image-url)
Table 5. Summary of relevant materials reported in the literature of multifunctional catalysts based on graphene for Li–O₂ batteries.

| Metal catalyst | Material (a) | Synthesis | Electrolyte | Discharge capacity (discharge rate) | Capacity limitation | Cycles (discharge rate) | Ref. |
|----------------|-------------|-----------|-------------|-------------------------------------|-------------------|------------------------|------|
| Noble metals   |             |           |             |                                     |                   |                        |      |
| PdFe alloy     | PdFe/N-rGO  | modified Hummer’s method + N doping by annealing in ammonia atmosphere + simultaneous chemical reduction or N-rGO and Fe/Pd precursors | 1 M LiTFSI in TEGDME | 22.905 mAh g⁻¹ (200 mA g⁻¹) | 1000 mAh g⁻¹ | 300 | [41] |
| Ru            | Ru-FeCoN/rGO | simultaneous heat treatment of rGO, Fe/Co precursors and melamine + Ru incorporation by heat treatment in presence of Ru precursor | 1 M LiTFSI in TEGDME | 11.431 mAh g⁻¹ (200 mA g⁻¹) | 600 mAh g⁻¹ | 200 | [90] |
| Ir            | IrO₂/Co-N-rGO | simultaneous heat treatment of rGO, Co precursor and melamine + IrO₂ incorporation by hydrothermal treatment | 1 M LiTFSI in TEGDME | 13.500 mAh g⁻¹ (200 mA g⁻¹) | 1000 mAh g⁻¹ | 45 | [96] |
| Transition metals |             |           |             |                                     |                   |                        |      |
| Ti            | Fe–TiO₂/N-GO | pyrolysis of GO in the presence of melamine + colloidal precipitation of ferrate and titanate + annealing at mild temperature | 1 M LiTFSI in TEGDME | 13.500 mAh g⁻¹ (200 mA g⁻¹) | 1000 mAh g⁻¹ | 30 | [100] |
| Fe            | Fe–Fe₃C/3D porous N-GO | hydrothermal synthesis of Fe-C + ball milling with melamine + high-temperature pyrolysis | 1 M LiTFSI in TEGDME | 7.500 mAh g⁻¹ (0.1 mA cm⁻²) | 800 mAh g⁻¹ | 30 | [100] |
| Fe–N–C/graphene sponge | | pyrolysis of pyrrolidinophthalocyanine at 450°C | 1 M LiPF₆ in TEGDME | 5.300 mAh g⁻¹ (50 mA g⁻¹) | 1600 mAh g⁻¹ | 50 | [101] |
| Co            | Co₃N-MWCNTs | thermal treatment of PANI catalyzed by Co species and MWCNTs | 1 M LiPF₆ in TEGDME | 3.700 mAh g⁻¹ (50 mA g⁻¹) | – | 50 | [104] |
|               |             | biphase N-doped Co/MWCNT | thermal treatment of Co 2-methyl imidazole crystals + thermal treatment in N₂/NH₃ atmosphere | 1 M LiCF₃SO₃ in TEGDME | 5.98 mAh cm⁻² (0.1 mA cm⁻²) | 1 mAh cm⁻² | 30 | [105] |
|               |             | Co₃O₄/N-graphene | 3D graphene grown on Ni foam by thermal treatment + ammonia evaporation induced method in the presence of Co₃O₄ precursor | 1 M LiTFSI in TEGDME | 19.133 mAh g⁻¹ (200 mA g⁻¹) | 1000 mAh g⁻¹ | 70 | [107] |
|               |             | CeO₂/N-rGO | hydrothermal treatment of GO and ammonium hydroxide + incorporation of CeO₂ by sol-gel method + hydrothermal process | 1 M LiTFSI in TEGDME | 18.866 mAh g⁻¹ (200 mA g⁻¹) | 1000 mAh g⁻¹ | 40 | [108] |
| Spinel        | NiCo₂O₄     | flowerlike NiCo₂O₄/N-GO | modified Hummer’s method + simultaneous hydrothermal reduction of GO, ammonium hydroxide, and Ni/Co precursors | 1 M LiTFSI in TEGDME | 15.046 mAh g⁻¹ (200 mA g⁻¹) | 1000 mAh g⁻¹ | 50 | [112] |

[a] PANI = polyaniline.
The use of nanostructures, based on an interconnected network of cages formed by less than five layers of graphene, presented superior cycling performance to that of traditional carbon black. The addition of Pt nanocatalyst decreased the charge overpotential, due to the smaller size of the generated discharge products and its more amorphous nature.

As discussed in Section 2.2, the high cost of Pt triggered the exploration of cheaper metal catalysts, such as Pd 3d transition-metal-based alloys. Leng et al. analyzed the effect of doping with different metals in the PdM alloy (M = Fe, Co, Ni) by using a nitrogen-doped rGO support. Palladium resulted in a lower charge overpotential, whereas PdCo and PdNi alloys showed a more limited catalytic activity due to metal dissolution upon cycling. PdFe alloy/N-rGO composite showed excellent cyclability (400 cycles at 400 mA g⁻¹), as observed in Figure 11a and b. This was attributed to the bifunctional nature of this cathode, in which the alloy was active during the OER, while the graphene material catalyzed the ORR. The use of Ru NPs on multielement (N-Fe-Co) codoped graphene results in interesting catalytic properties and excellent cycling behavior (Figure 11c, d). The introduction of different elements within the graphene network results in a higher number of defects and provides a greater amount of graphitic carbon.

Multielement N–Co graphene matrix has been used as a support for IrO₂ NPs. The high surface area of graphene, enhanced ORR activity due to Co and N, and the high dispersion of IrO₂ NPs improved the capacity retention (reversible capacity: 11731 mAh g⁻¹). Nazarian-Samani et al. studied Ru quantum dots on N-doped holey graphene; they observed the positive effect of Ru as the OER catalyst and its role in the creation of structural defects. In the formation of Ru/graphene composites, it was also possible to add other carbonaceous nanostructures, such as single-walled carbon nanotubes (SWNTs), to stabilize the cathode structure. Initially, a cross-linked gel of SWNTs–single-layer graphene was synthesized by using an ion liquid that was extracted in a controlled manner. This material presented an acceptable cycling stability (75 cycles), although after the 25th cycle the accumulation of Li₂CO₃ resulted in an increase in the overpotential. By renewing the atmosphere with O₂, it was possible to recover the air electrode up to 100 cycles. Another effective strategy exploited by Guo et al. focused on encapsulating RuO₂ NPs in nanoporous N-doped graphene. The RuO₂ catalyst contributed to improving the kinetics of the OER with a low charge potential (< 4.05 V), and the fact of being encapsulated favored a uniform dispersion in the composite.

TiO₂ has been also proposed due to its lower price, high chemical stability, and high catalytic activity. Yang et al. doped this material with Fe³⁺ cations to modify the electronic state, and thus, increase the electronic conductivity of TiO₂. In this way, Fe³⁺-doped TiO₂ became a p-type semiconductor.

Figure 11. a) Plots of the terminal voltage of the batteries and b) specific capacities versus cycle number with PdM/N-rGO (M = Fe, Co, Ni) catalysts. Reproduced from Ref. [41] with permission. Copyright 2017, Elsevier. The charge–discharge cycles of Li–O₂ cells with Ru–FeCoN/rGO (c) and the corresponding specific energy efficiency (d). Reproduced from Ref. [89] with permission. Copyright 2015, Royal Society of Chemistry.
with a greater amount of O vacancies, which translated into a positive effect on the catalytic activity.\textsuperscript{[96]} The Fe–TiO\textsubscript{2}/N-doped graphene composite presented an important catalytic activity that gave rise to a lower overpotential (0.83 V). In addition, the cell presented a good capacity retention during 5 cycles and acceptable cyclability up to 45 cycles. TiO\textsubscript{2}/graphene composites have also been tested as high-power LIB electrodes with a surface amorphization that facilitates the diffusion of lithium.\textsuperscript{[97]} Other authors focused their studies on the development of Fe-based catalysts supported on N-doped graphene. Li et al. used a cobalt-containing metal–organic framework (MOF) as a template to prepare transition-metal/N/C ORR catalysts (Figure 12a,b).\textsuperscript{[98]} The composite included graphene nanotubes produced by means of CVD with Ni nanowire templates. The ratio of pyridinic to quaternary nitrogen is related to the catalytic behavior and could be adjusted by controlling the temperature of the CVD treatment. The sample heated at 1000 °C yielded the highest amount of pyridinic nitrogen and presented the greatest catalytic activity during the ORR.\textsuperscript{[99]} The use of MOF templates for producing carbon-based nanocomposites with unique morphologies was also the strategy followed to prepare Fe/Fe\textsubscript{3}O\textsubscript{4}/graphene composites.\textsuperscript{[100]} With this MOF-based template, and melamine as a source of C and N, it was possible to obtain 3D porous N-doped graphene with a very high proportion of meso-/macropores. This morphology avoided the irreversible phase-to-face restacking of graphene and was stable for 30 cycles. Another way to increase the cyclic performance is to assemble Fe–N–C composites on a 3D structure of a graphene sponge (Figure 12c).\textsuperscript{[101]} In this case, graphene formed an optimal framework for the dispersion of catalyst NPs, and thus, a clear effect was observed during the OER that seemed to be related to its special molecular geometry. The [Fe–4N] species, if bound to the carbonaceous support, maintained a planar coordination, which allowed Fe to present two free orbitals for bonding with oxygen from the LiOO\textsubscript{2} molecule, without breaking the O–O bond. Park et al. developed a composite based on N-doped exfoliated graphene, together with α-MnO\textsubscript{2} nanotubes,\textsuperscript{[102]} for which the introduction of N atoms increased the ORR kinetics (Figure 12d).

Wu et al. analyzed cobalt-based catalysts to obtain highly graphitized carbon nanostructures from PANI heteroatom polymer.\textsuperscript{[104]} This cathode presented stable cycling during 20 cycles, although from the 30th cycle a loss of capacity was detected. This loss is caused by the accumulation of discharge products that are not decomposed during charging, which block the active sites. Tan et al. resorted to the use of cobalt-containing MOFs for the production of N-doped Co/graphene multicapsules.\textsuperscript{[105]} In this composite, the presence of N and Co atoms in graphene provided a greater number of active sites, together with a large porosity, which improved the electrocatalytic activity. Another strategy included the preparation of graphene decorated by Co@CoO NPs, to which the addition of core–shell particles had a clear effect on increasing the capacity and cyclability (up to 70 cycles at 100 mA g\textsuperscript{−1}).\textsuperscript{[106]} Cobalt oxides are the most actively investigated materials in multifunctional graphene-based catalysts. For instance, CoO and Co\textsubscript{3}O\textsubscript{4} hollow NPs have been used to manufacture composites on N-doped graphene (Figure 12e,f).\textsuperscript{[103]} Although the catalytic effect of cobalt is not very clear, the addition of an n-type carbon dopant, such as nitrogen, leads to a certain disorder in the carbon nanostructures, which facilitates the ORR. An investigation of 3D graphene–Co\textsubscript{3}O\textsubscript{4} NPs supported on Ni foam resulted in improved kinetics of the ORR and OER through the presence of Co\textsubscript{3}O\textsubscript{4}.\textsuperscript{[107]} More than 60 stable cycles were obtained; however, it was important to control the distribution of Co\textsubscript{3}O\textsubscript{4} due to its restricted electronic conductivity. A design based on 1D nano-

Figure 12. Representative TEM images of N-Fe MOF/graphene catalyst, showing a typical graphene tube (a); the open mouth of a graphene tube is marked by a yellow arrow (b). Reproduced from Ref.\textsuperscript{[98]} with permission. Copyright 2014, Wiley-VCH. c) Photograph of the graphene sponge after being moistened with DMSO solvent. Reproduced from Ref.\textsuperscript{[101]} with permission. Copyright 2014, Elsevier. d) SEM image of MnO\textsubscript{2} nanotube/N-doped thermally exfoliated graphene composite electrode. Reproduced from Ref.\textsuperscript{[102]} with permission. Copyright 2013, Electrochemical Society. SEM (e) and TEM (f) images of Co N-doped graphene composite. Reproduced from Ref.\textsuperscript{[103]} with permission. Copyright 2015, Wiley-VCH.
structures seems to be the most suitable in this type of system because it facilitates a continuous pathway for electron transport, in addition to providing numerous accessible active sites due to the high surface to volume ratio.

CeO$_2$ is an alternative redox catalyst that can promote both the ORR and OER. NPs of this material can be dispersed uniformly over N-doped graphene to give a composite with an acceptable cycling performance during 40 cycles; from cycle 20th, however, the charge potential increases through the accumulation of byproducts (lithium formate, acetate, and carbonate, mainly). This material has also been tested in the form of nanoflakes, with the observation of a certain ORR activity, but poor cyclability. In contrast, the ORR activity of ZnO nanofibers on graphene was limited and only 10 cycles were delivered at 210 mA g$^{-1}$ with a small decrease in the overpotential.

Among other systems studied, molybdenum sulfides in the form of NSs on highly porous rGO aerogel have been investigated. By adjusting the component proportion in MoS$_2$/rGO to 1:2, it was possible to considerably increase not only the capacity, but also the cycling stability. However, the addition of MoS$_2$ had no noticeable effect on the ORR or OER. In addition, the response of the composite at high current densities (0.5 mA cm$^{-2}$) was very poor. Spinel compounds have also been deposited on multifunctional matrices. Thus, nanostructured NiCo$_2$O$_4$ in the form of a chrysanthemum flower was combined with N-doped rGO to obtain a bifunctional catalyst. The addition of rGO sheets to the composite favored four-electron transfer during the ORR, as well as the spinel phase promoting greater OER kinetics as a result of the presence of mixed-metal valences. In this way, a greater capacity due to an increase in the number of active sites was obtained, but there was no relevant improvement in the decrease of the cycling overpotential. In addition to the spinel structure, perovskite-type materials are also very attractive in the design of catalytically active compounds. Kim et al. utilized GNP as a support for Nd$_{0.5}$Sr$_{0.5}$CoO$_{2-x}$ nanorods. This composite presented a clear synergy between both materials in which the OER activity, which was superior to that of the Pt/C reference material, was provided by spinel particles, while improved ORR kinetics was achieved by the use of graphene as a support.

3. Sodium–Oxygen Batteries

Research into graphene-based air electrodes has emerged due to the promising features of this tunable material for Na–O$_2$ technology (Table 6). The use of graphene was first examined by Liu et al., who achieved a discharge capacity as high as 9268 mAh g$^{-1}$ (200 mA g$^{-1}$) with GNSs; this value was almost three times higher than that of typical gas diffusion layers. The performance of N-GNSs was studied and compared with that of prismatic GNS by Li et al. They found that the presence of nitrogen in the carbon network resulted in an excellent electrocatalytic activity towards the ORR, delivering a discharge capacity almost two times greater than that of undoped GNS (8600 and 4350 mAh g$^{-1}$ at 75 mA g$^{-1}$, respectively). As reported for Li–O$_2$ batteries, this improvement can be assigned to the introduction of defective sites by nitrogen doping and the ability of nitrogen atoms to tailor the morphology of discharge products, resulting in the formation of small and uniformly distributed NaO$_2$ particles. Furthermore, the effect of a hierarchical macroporous framework on the electrochemical performance of rGO electrodes was reported by Liu et al. The 3D arrangement of cathodes showed an improved areal capacity compared with that of traditional carbon electrodes (12 vs. 3 mA cm$^{-2}$) due to a dense and continuous growth of discharge products. The large size of mesopores, relative to that of mesoporous materials, prevented pore clogging and, consequently, early cell failure. Also, Enterría et al. studied the influence of porosity on electrochemical performance by using rGO aerogels prepared by freeze-drying and thermal reduction of GO suspensions. The porosity and orientation of the graphene sheets was tuned by adjusting the freezing temperature of the GO suspension. The best electrochemical performance was achieved for the lowest freezing temperature ($-196^\circ$C), delivering a discharge capacity of 6.61 mAh cm$^{-2}$ (100 mA g$^{-1}$) and 40 cycles under a capacity limitation regime of 0.5 mA cm$^{-2}$ (Figure 13a). Hence, a random orientation of the

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**Table 6. Summary of relevant materials in the literature for graphene-based materials for Na–O$_2$ batteries.**

| Material | Synthesis | Electrolyte | Discharge capacity (discharge rate) | Capacity limitation | Cycles (discharge rate) | Ref. |
|----------|-----------|-------------|------------------------------------|---------------------|-------------------------|-----|
| GNS      | Hummer’s method | 0.25 M NaPF$_6$ in DME | 9268 mAh g$^{-1}$ (200 mA g$^{-1}$) | 1200 mAh g$^{-1}$ | 10 | [114] |
|          | + casting GO on stainless-steel mesh | | | | | |
|          | + freeze-drying | | | | | |
| N-GNS    | Hummer’s method | 0.5 mol dm$^{-3}$ Na$_2$SO$_4$CF$_3$ in DEGDME | 6000 mAh g$^{-1}$ (75 mA g$^{-1}$) | 1150 mAh g$^{-1}$ | 3 | [115] |
|          | + annealing at mild temperature | | | | | |
| porous rGO | coating Ni foam with graphene colloids | 0.25 M NaClO$_4$ in DME | 12 mA cm$^{-2}$ (0.1 mA cm$^{-2}$) | 1 mA cm$^{-2}$ | 17 | [116] |
| Pt/GNS   | in situ growth of Pt particles on GO by hydrothermal treatment | 1 M NaClO$_4$ in PC | 7574 mAh g$^{-1}$ (0.1 M cm$^{-2}$) | 100 mA g$^{-1}$ | 10 | [117] |
| Ag/rGO  | simultaneous reduction of Ag precursor and GO using ethylene glycol | 1 M NaPF$_6$ in TEGDME | 566 mAh g$^{-1}$ (0.1 M cm$^{-2}$) | 0.125 mA cm$^{-2}$ | 30 | [88] |
| rGO aerogels | freeze-drying of commercial GO | 0.1 M NaClO$_4$ in DME | 6.61 mAh cm$^{-2}$ (0.25 mA cm$^{-2}$) | 0.5 mA cm$^{-2}$ | 40 | [7] |
|          | + annealing at high temperature | | | | | |
graphene sheets, originated by sudden freezing, minimized re-stacking of the graphene sheets during self-assembly. This specific 3D arrangement enhanced the accessibility of the reactants towards the active sites in defects and edges, and provided much better performance than that of other aerogels (Figure 13b).

The synergetic effect between graphene-based materials and transition-metal catalysts has also been explored for Na–O₂ batteries to improve the kinetics of both the ORR and OER. Zhang et al. reported the incorporation of Pt NPs on GNSs by a simple hydrothermal method. The high electrocatalytic activity of the Pt/GNS composite delivered a high discharge capacity of 7574 mAh g⁻¹. Kumar et al. anchored Ag NPs onto a graphene matrix by simultaneous chemical reduction of GO and AgNO₃. The composite yielded discharge capacity values of 566, 136, and 87 mAh g⁻¹ at 0.1, 0.2, and 0.3 mA cm⁻², respectively. NaO₂, Na₂O₂, and Na₂O were identified as stable discharge products and discharge capacities of around 130 (0.13) and 70 mAh g⁻¹ (0.06 mAh cm⁻²) were attained over 30 cycles.

4. Summary and Outlook

Metal–O₂ batteries have the capability to play an important role in the development of next-generation energy-storage systems, due to their high theoretical energy density relative to that of current systems (e.g., LiBs). To date, the full potential of these batteries has not yet been achieved due to challenges associated with the metal anode, air cathode, and electrolyte. One of the main challenges to make these systems commercially available is the sluggish kinetics of the ORR/OER. The rational design of the air electrode can, therefore, reduce losses due to these reactions.

At this point, graphene stands out to lead a new generation of batteries with enhanced performance, thanks to its outstanding properties, such as large surface area, high electronic conductivity, and high electrochemical stability. In the last 15 years, the majority of research has been conducted at the laboratory scale, with the aim of implementation in real applications. However, the commercialization of graphene materials has increased enormously from the laboratory scale to several companies producing this material. The market leaders are those working in corrosion and wear-resistant coatings; applications in energy storage have yet to be implemented. The next step will come from a need from the commercial sector in a suitable application (e.g., electric vehicles), and graphene producers will have to meet the demands of the graphene material, depending on the use.

Herein, enormous progress on the utilization of graphene-based cathode materials for Li and Na–O₂ batteries has been summarized and the limitations regarding these cathodes discussed. Regarding Li–O₂ batteries, the use of pure graphene has been widely investigated with the aim of tuning its porosity and morphology to enhance oxygen diffusion and provide active sites for the nucleation of discharge products. However, the OER kinetics are still sluggish and graphene–metal composites with Ru, Pt, Ni, Co, Cu, Pd, Au, and Ir have been investigated. Nevertheless, the high price of these materials has led to research into earth-abundant elements, such as cobalt, aluminum, and manganese oxides and spinel compounds. In addition, the introduction of heteroatoms and further doping with metals and/or oxides into the graphene structure has led to interesting results. Heteroatoms, of which the most studied and efficient systems are those based on nitrogen, act as active centers for the ORR/OER and, at the same time, generate defects in the graphene network. Although modified graphene results in major improvements during the ORR, its effect on OER is very limited. To overcome this drawback, a subsequent strategy was based on the addition of elements (noble metals, oxides, etc.) that favored the OER.

Regarding Na–O₂ batteries, research is less extensive due to the novelty of the technology (first reported in 2012). Work has focused on pure graphene materials based on GNSs and rGO, as well as nitrogen and platinum doping, similar to research reported for Li–O₂ batteries. However, there is still a long path to explore in this field.

It is important to highlight the optimal stability of graphene during cycling, in contrast to commonly used carbon-based materials, which present poor stability at high current densities. This is ascribed to the 2D structure of graphene and its outstanding electronic conductivity. The formation of parasitic products under these conditions is kinetically limited, which provides graphene with excellent charge/discharge cycling stability. The selection of an optimal electrode design, and the proper formulation of the graphene/catalyst composite, lead
to a superior catalytic activity, which results in a substantial decrease of the overpotential and enhanced cycling performance. For future research in this field, we herein present some perspectives to boost the practical application of these devices. The ideal air electrode must present desirable bifunctional catalytic activities towards the ORR and OER. Graphene, thanks to its planar structure, facilitates the impregnation of the electrolyte and the diffusion of oxygen through its channels. In addition, the large number of active sites favors electrochemical reactions, mainly the ORR. Regarding the OER, the decomposition of as-generated discharged products can be promoted by an effective electrocatalyst, with those related to spinel structure being the most promising. In this sense, a deep understanding of the effect of different catalytic phases on the graphene surface will enable a rational design of high-performing air cathodes that address the challenge of rechargeability by improving the kinetics of the ORR/OER and suppressing side reactions. It is necessary to perform advanced characterizations to elucidate the reaction mechanisms by means of ex situ and, in particular, in situ techniques. Thus, structural and physicochemical changes that occur upon charging and discharging can be understood. The engineering of future graphene-based cathodes should be oriented to the control of the growth and decomposition of discharged products and the three-phase boundary reaction areas. For this purpose, a combination of ex situ, in situ, and operando techniques needs to be undertaken to understand how the formation of defects and vacancies in graphene affects the nucleation and subsequent decomposition of the discharge products. Multifunctional graphene cathodes are potential electrocatalysts in M–O2 batteries. A maximized efficiency during the ORR and OER can be achieved by further exploration of the synergistic effect between the 3D structure, porosity, defects, and catalyst particles/atoms on the surface of the graphene-based air cathodes. It is necessary to develop realistic models that correlate the morphology of the material and its formulation with cell performance.

Finally, realistic processing and environmentally friendly and low-cost preparation methods should be considered in the design of graphene-based electrodes with a view to future scalability.

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**Conflict of interest**

The authors declare no conflict of interest.

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