REVIEW

The application of carbon materials in nonaqueous Na-O$_2$ batteries

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Abstract

Na-O$_2$ batteries are advantageous as the candidates of next-generation electric vehicles due to their ultrahigh theoretical energy density and have attracted enormous attention recently. Tremendous efforts have been devoted to improve the Na-O$_2$ battery performance by designing advanced electrodes with various carbon-based materials. Carbon materials used in Na-O$_2$ batteries not only function as the air electrode to provide active sites and accommodate discharge products but also as Na anode protectors against dendrite growth and chemical/electrochemical corrosion. In this review, we mainly focus on the application of various carbon-based materials in Na-O$_2$ batteries and highlight their advances. The scientific understanding on the fundamental design of the material microstructure and chemistry in relation to the battery performance are summarized. Finally, perspectives on enhancing the overall battery performance based on the optimization and rational design of carbon-based cell components are also briefly anticipated.

KEYWORDS
air electrode, carbon materials, nonaqueous Na-O$_2$ batteries, sodium anode

1 | INTRODUCTION

With the excessive depletion of nonrenewable fossil fuels and increasing environmental concerns, development of green and sustainable energy is of considerable significance in the modern society. Although renewable solar and wind energy resources have shown promising potential to reduce the dependence on fossil fuels, their application still face serious challenges due to the low performance and controllability.[1] Secondary batteries based on electrochemical oxidation/reduction reactions are considered to be one of the most reliable energy solutions for environmental concerns. Therefore, several energy-storage systems such as lead-acid, nickel-metal hybrid, and lithium-ion batteries have been extensively studied in the last few decades, and the success of lithium-ion batteries has contributed to the advancement of portable electronic devices.[2,3] However, the energy density of the currently available commercial batteries cannot satisfy the stringent demands of next-generation electric vehicle (EV) transportation, and the development of high energy density storage technologies is urgent for widespread adoption of EVs.[4-6]

Metal-O$_2$ batteries with high theoretical energy densities have been developed under these conditions. Among various metal-O$_2$ battery technologies, Li-O$_2$ battery system has captured enormous attention due to its extremely high energy density (3500 Wh kg^{-1}), which is comparable with gasoline combustion systems.[7-9] However, the practical application of Li-O$_2$ batteries has

been hindered by scientific and technological limitations such as high charge overpotential and serious parasitic reactions, which severely deteriorate the cell performance.[9-13] As an alternative to Li-O₂ battery system, Na-O₂ batteries do not suffer from the negative effects of high charge overpotential even with pure carbon cathodes.[14-16] The theoretical energy densities of Na-O₂ batteries are calculated to be 1602 and 1105 Wh kg^{-1} based on the formation of Na_2O_2 and NaO_2, respectively, which is around six to nine times higher than that of Li-ion batteries. With these advantages, as well as the low cost and natural abundance of sodium metal, Na-O₂ batteries show great application potential for EV transportation.

Although Na-O₂ batteries are still at its initial stage of development, impressive breakthroughs have been achieved in recent years.[5,17] Along with the extensive efforts toward exploring the electrochemistry of Na-O₂ batteries, much attention has been devoted to the design of the air electrode because its efficiency plays a crucial role in determining the overall cell performance.[18-21] Carbon materials have been widely applied in various energy-storage systems due to their good electrical conductivity, versatile porous nanostructure, high chemical stability, and low cost, and are considered as the most popular candidates to construct efficient air electrodes for Na-O₂ batteries. Carbon-based air electrodes with porous structure can provide active sites for oxygen reduction/evolution reactions and facilitate sufficient mass transport of O_2/Na^+ in Na-O₂ batteries. Further, the void space in the carbon cathode are ideal for the accommodation of discharge products. More recently, the feasibility of using carbon materials to mitigate the Na dendrite growth and alleviate the Na corrosion has also been demonstrated, and the roles that carbon materials play are evolving from a sole air electrode to functional core components in Na-O₂ batteries.[22,23]

Therefore, in this review, we intend to introduce the recent advancements toward improving the electrochemical performance of Na-O₂ batteries via rational design of electrodes using carbon-based materials. First, the reaction mechanism of Na-O₂ electrodes, as well as the key issues of electrodes that may result in the cell performance deficiency are systematically introduced. The discussion on the structural design and advantages of carbon materials used in Na-O₂ batteries, from the air electrodes to anode protection, will be sequentially presented in the following sections. Finally, the remaining challenges and future perspectives for the development of high-performance Na-O₂ batteries with carbon materials are proposed. We believe that this review will inspire the design of highly efficient electrodes for stable Na-O₂ batteries and promote the future practical application of this promising technology.

2 | PRINCIPLE OF A NONAQUEOUS NA-O₂ BATTERY

2.1 | Electrochemistry of a nonaqueous Na-O₂ battery

A typical nonaqueous Na-O₂ battery is composed of a sodium metal anode, a porous oxygen-breathing cathode, and a separator filled with Na^+-conducting electrolyte. A schematic illustration of a typical nonaqueous Na-O₂ cell configuration is shown in Figure 1.

Different to the reversible intercalation of Na^+ between the cathode and the anode in Na-ion batteries, the energy in Na-O₂ batteries is stored and released based on conversion reactions. During the discharge process, sodium metal is oxidized to sodium ions (Na^+), which migrate to the cathode through the organic electrolyte. At the same time, the O_2 is reduced on the cathode surface to form reduced oxygen species (O_2^- or O_2^{2-}), and then combine with migrated Na^+ to form metal oxides as the discharge products. When the cell is charged, the reactions will proceed in the reverse direction with Na metal plating at the anode and oxygen evolving at the cathode. While unlike the formation of Li_2O_2 as the major discharge product in Li-O₂ batteries, there are two discharge products (NaO_2 and Na_2O_2) produced in Na-O₂ battery system.[24,25] The associated reaction equations can be briefly presented as follows:
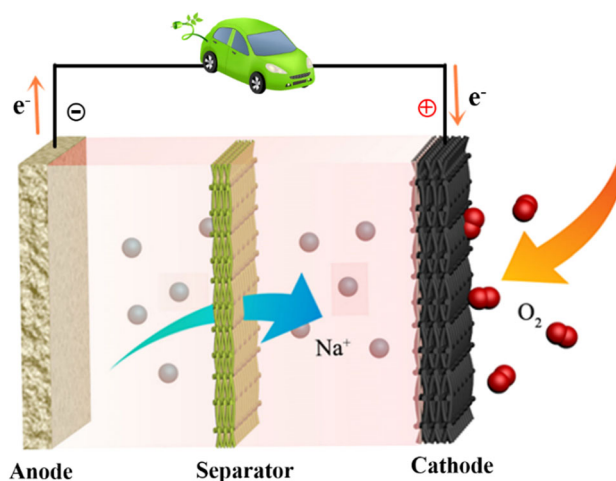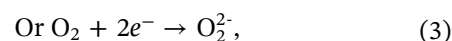
$$\text{Negative electrode: Na} \rightarrow Na^+ + e^-, \tag{1}$$

$$\text{Positive electrode: } O_2 + e^- \rightarrow O_2, \tag{2}$$

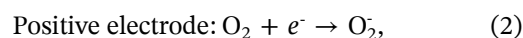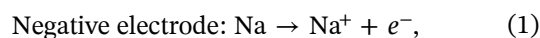$$\text{Or } O_2 + 2e^- \rightarrow O_2^{2-}, \tag{3}$$

FIGURE 1 Schematic illustration of a nonaqueous Na-O₂ cell configuration

Overall: $Na + O_2 \rightarrow NaO_2$; $E^0 = 2.27\,V$, \hfill (4)

Or $2Na + O_2 \rightarrow Na_2O_2$; $E^0 = 2.33\,V$. \hfill (5)
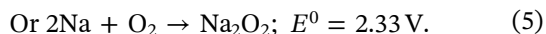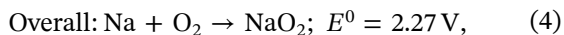
In the Na-O$_2$ batteries, oxygen reduction reaction (ORR) can proceed via a one-electron pathway or a two-electron transfer process with the formation of NaO_2 or Na_2O_2, respectively. The formation of Na_2O_2 delivers drastically higher theoretical energy density (1605 Wh kg^{-1}) compared with that of NaO_2 (1108 Wh kg^{-1}).[26] In contrast, peroxide-based Na-O$_2$ batteries suffer from the high charge over-potential (>1 V), which is comparable with that of Li-O$_2$ cells.[5,27,28] The electrochemical performance of Na-O$_2$ batteries is greatly affected by the nature of discharge products, and controlling the formation of desired Na-O compounds is crucial for achieving high-performance Na-O$_2$ batteries. Although both NaO_2 and Na_2O_2 have been predicted as the main discharge products of Na-O$_2$ batteries by using theoretical computational techniques, it is still very difficult to identify which product is more favorably produced based solely on the thermodynamic data.[29,30]

Experimentally, important progresses have been made in terms of electrochemistry of Na-O$_2$ batteries under certain conditions, and some of the physicochemical factors that affect the reaction pathway of Na-O$_2$ batteries have been investigated. First, the nature of the electrolyte (solvent) has a profound effect on the electrochemistry of Na-O$_2$ batteries. As reported in previous report, distinct to the formation of NaO_2 via solution-mediated route in the solvents with a high donor number (DN), low DN solvents incapable of forming an ion pair with O_2^- intermediates, and consequently contribute to the formation of Na_2O_2 on the Au electrode surface via further oxidation of O_2^-.[31] Therefore, controlling of the mechanistic direction of discharge process (sodium superoxide or sodium peroxide) with different electrolytes may enhance the ability to tailor the energy density of Na-O$_2$ batteries. Besides, the chemical stability of electrolyte against O_2^- attack is also crucial for the cell performance. The formation of $Na_2O_2 \cdot 2H_2O$ due to degradation of NaO_2 in the organic electrolyte has been reported in several groups, and electrolyte solvents with high acid dissociation constants (pK_a) are considered beneficial to the formation of NaO_2.[32,33] Except for electrolyte, surface chemistry and electrocatalytic activity of carbon-based cathodes also play substantial role in the electrochemical reaction paths. The discharge product of commercial H2315 carbon paper (CP) cathode has been widely reported to be NaO_2 cubes.[14,15] After introducing Pd nanoparticles on the CP cathode, two-electron electrochemical process occurs with the formation of $Na_2O_2 \cdot 2H_2O$ as the discharge product.[26] In our recent study, we found that the presence of oxygen functional groups (–COOH, –OH,

etc) in hydrophilic CP cathode can also facilitate the growth of peroxide-based discharge product through a surface-mediated mechanism.[34] In fact, aside for the composition and formation mechanism of discharge products, the morphology of NaO_2 also can be tuned by changing the properties of solvents and air electrodes.[35-37] Previous studies reported that the trace of H_2O additives in the electrolyte can be beneficial for the cell discharge capacity by promoting the solution-mediated growth of NaO_2 crystals.[38,39] However, it should be noted that water in the electrolyte tends to react with NaO_2 to produce $Na_2O_2 \cdot 2H_2O$ and NaOH during the discharge process or at rest.[40] Moreover, the high content of humidity in the gas atmosphere also contributes to the formation of hydroxide as well as poor cell performance.[41,42]

In fact, the formation of peroxide in Na-O$_2$ batteries is highly related to the presence of O_2^- intermediates and their further reduction via chemical or electrochemical pathways. The minor difference in the operating parameters of Na-O$_2$ batteries helps to explain the origin of discharge products diversity in different groups. When compared with the intensive investigation on Li-O$_2$ batteries, the research and understanding of the electrochemistry on the Na-O$_2$ battery is far from complete and more fundamental research is required in future studies.

2.2 | The fundamental challenges of electrodes in Na-O$_2$ battery

Although Na-O$_2$ batteries have shown great potential as an emerging energy-storage system due to its high theoretical energy density and environmental safety, several key challenges still need to be addressed before its commercialization. The operating atmosphere (humidity and gas contamination) is an important factor in affecting the nature of discharge products and the cell performance.[42] Recent studies have also reported that organic electrolytes are readily attacked by the oxygen species, such as O_2^- and $^1O_2$, to generate unfavorable side products, which is harmful to the reversible charge capacity and cycle life.[5] While it is widely accepted that the inefficiency of the air electrode and anode are primarily responsible for the low capacity, poor safety, and limited cycle life of state-of-the-art Na-O$_2$ batteries. The main challenges facing the development of cathode and anode in Na-O$_2$ batteries are highlighted as follows (Figure 2):

(1) Clogging of the air electrodes. The dominant discharge product of Na-O$_2$ battery (insulating Na_2O_2, NaO_2) are insoluble in the organic electrolyte, which will precipitate on the surface or within the pores of the air electrode during discharge. Meanwhile, the limited solubility and low diffusivity of O$_2$ in the electrolyte
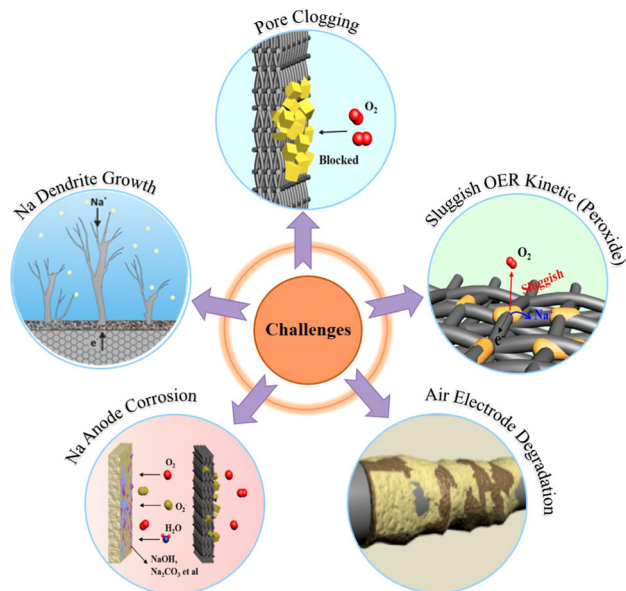
FIGURE 2 The key issues of electrodes in nonaqueous Na-O₂ batteries (Reproduced with permission from Reference,[18] Copyright 2015, Royal Society of Chemistry. Reproduced with permission from Reference.[46] Copyright 2017, Wiley-VCH). OER, oxygen evolution kinetics

result in the relative higher local charge density distribution on air electrode near the O_2 reservoir. Consequently, the discharge products will preferentially deposit at the air electrode that face the oxygen reservoir.[43] Such a distribution of the discharge products potentially clog the pores at the oxygen side and further block the O_2/Na^+ transport pathways.[14,23] Therefore, the achievable discharge capacity is much lower than the theoretical value due to the termination of discharge process before the void volume of air electrode is fully utilized.[23]

(2) Sluggish electrochemical oxidation kinetics of Na_2O_2. With the formation of NaO_2, the Na-O₂ batteries can be recharged with a low charge overpotential even with the pure carbon cathodes.[14] However, when it comes to Na_2O_2 (mostly $Na_2O_2 \cdot 2H_2O$), sluggish electrochemical oxidation kinetic with high charge overpotential can be observed on carbon-based air electrodes.[26] On one hand, the high charge overpotential reduce the round-trip energy efficiency by requiring greater power to recharge than can be recovered during the discharge process. On the other hand, the high charge potential will trigger severe electrolyte decomposition and carbon corrosion, which are the important factors in the decline of the battery performance.[18]

(3) Air electrodes degradation. Carbon is widely used as the air electrode in Na-O₂ batteries. However, the reaction intermediate (O_2^-) and discharge products (Na_2O_2, NaO_2) are problematic species toward the

carbon cathode itself. Direct oxidation of carbon cathodes in the presence of solvated O_2^- and NaO_2 has been reported with the formation of various Na-carboxylate decomposition products on the cathode surface. The undesired decomposition of cathode binders induced by hydrogen abstraction of O_2^- partially contributes to the air electrode degradation.[37] Moreover, carbonate-based side products can be formed on the outer shell of NaO_2 cubes due to the instability of organic electrolyte against the NaO_2.[19,44] All those side products are hard to decompose during the subsequent charging process and will gradually cover the active sites of the carbon cathode, leading to a gradual increase in the charge overpotential, capacity fading during cycling, and limited cycle life.

(4) Uncontrollable Na dendrite growth. Uneven stripping/platting of Na metal can result in the formation of dendritic Na structures, which can penetrate the solid-electrolyte interphase (SEI) film. The repeated breakage and repair of the SEI layer induce continuous consumption of the electrolyte and Na metal, resulting in decreased coulombic efficiency along with increased interfacial resistance.[45] Premature cell death can be expected after the electrolyte or Na metal is eventually exhausted. Moreover, the accumulation of sharp Na dendrites may penetrate through the separator causing safety concerns over internal short circuits.[46,47]

(5) Na anode corrosion caused by contaminants crossover. The electrochemical power source of Na-O₂ batteries is based on conversion reactions, in which solvated O_2 and O_2^- intermediates are involved. The O_2/O_2^- crossover in Na-O₂ batteries can induce severe passivation/parasitic reactions on the Na metal anode.[23,47,48] The gradual accumulation of side products, such as NaOH, Na_2CO_3, and organic products, on the Na surface could result in blockage of Na^+ migration, increased polarization, and eventually battery failure. More recently, the generation of singlet oxygen ($^1O_2$) has been reported,[49] and parasitic chemistry involving migrated $^1O_2$ at the Na anode may also cause problems. Besides oxygen species (O_2, O_2^-, $^1O_2$), the Na anode can react with H_2O from electrolyte decomposition (or air) and further the Na degradation.[33,39] However, the currently used porous glass fiber separator in Na-O₂ batteries cannot block the diffusion of contaminants from the cathode to the Na anode.

Multiple and combined strategies have been reported to solve those problems: (a) designation of a conducting network with hierarchical porous structure to alleviate the pore clogging and facilitate continuous O_2/Na^+ transportation; (b) construction of air electrodes with sufficient electrocatalytic activities toward oxygen

evolution kinetics (OER); (c) application of carbon-free electrodes or surface protection of carbon by coating metal oxides to alleviate the carbon cathode degradation; (d) proper anode protection or adding electrolyte additives to minimize Na dendrite growth; (e) introduction of contaminants crossover impediments to alleviate/ mitigate Na corrosion; and (f) searching for a substitute for Na metal to tackle the Na-related problems. Among the various materials that can help to achieve the above strategies for enhancing the cell performance, carbon materials have shown great potential due to their unique properties.

In the following sections, we will mainly focus on the application of carbon-based materials in Na-O$_2$ batteries, from the air electrode to Na anode protector, and the advantages of carbon-based materials for achieving high-performance Na-O$_2$ batteries are highlighted. We expect to obtain a comprehensive understanding on the roles that carbon materials with different microstructure, surface property, and compositions play in enhancing the electrochemical performance of Na-O$_2$ batteries. More importantly, remaining issues are commented and possible directions for future work using carbon materials to improve the cell performance are prospected.

3 | CARBON-BASED MATERIALS FOR NA-O$_2$ BATTERY CATHODE

To achieve high-performance Na-O$_2$ batteries, using carbon nanomaterials as the cathode is advantageous due to their good electronic conductivity, tunable porous structure, good chemical stability, lightweight, and low cost. As the discharge products of Na-O$_2$ batteries, mainly NaO$_2$ and Na$_2$O$_2$, are electronically insulating and insoluble in organic electrolytes, many important properties have to be considered when designing a highly efficient carbon-based air electrode for Na-O$_2$ batteries. For example, the air electrodes should have a high electronic conductivity to facilitate electron transportation, sufficient pore volume for discharge products accommodation, and optimized pore structure for rapid Na$^+$/O$_2$ mass transportation. Sufficient mechanical strength to tolerate the volume expansion during the formation and decomposition of solid discharge products is also required. Additionally, the NaO$_2$ and Na$_2$O$_2$ are strong oxidizers, and thus air electrodes should be stable against the discharge products oxidation and, at the same time, not promote the parasitic reactions involving the organic electrolyte and discharge products.

So far, a large number of hierarchical porous carbon-based cathodes have now been developed to alleviate the pore-clogging problem.[16,50] Additionally, inspired by the utilization of electrocatalysts to lower the charge over-potential in Li-O$_2$ batteries, air electrode optimization through heteroatoms doping and catalyst attachment has also been developed to enhance the OER kinetics in peroxide-based Na-O$_2$ batteries.[51-53] The main focus of this section is the efficacy of various carbon-based cathodes with unique architecture and chemical properties, and the relationships between the cell performance and air electrode properties will also be discussed.

3.1 | Pristine carbon materials

A room-temperature rechargeable Na-air battery was first reported by Fu and co-workers by using a diamond-like carbon (DLC) thin film as the oxygen electrode.[54] The DLC thin film cathode can deliver an initial discharge capacity of 1884 mAh g^{-1} at 1/10 C-rate, and Na$_2$O$_2$ and Na$_2$CO$_3$ were detected as the discharge products of the constructed cell with carbonate-based electrolyte. Kwak et al[55] synthesized the ordered mesoporous carbon (OMC) and evaluated as a nanostructured conductive matrix to accommodate the nonconductive discharge products in Na-O$_2$ batteries. The high surface area and pore volume of endow Na-O$_2$ battery deliver an initial discharge capacity of 7987 mAh g^{-1} at 100 mA g^{-1}, which is significantly higher than the 4864 mAh g^{-1} of super P electrode.

To give a more holistic view on the rechargeability and reaction kinetics of Na-O$_2$ batteries, a series of carbon cathodes with specifically designed surface area and porous structure were synthesized by our group using a heat-treatment procedure, as shown in Figure 3A.[56] The result indicates that the cell discharge capacity has a linear relationship with the cathode-specific surface area as a higher surface area provides more active sites to facilitate ORR and enables insoluble discharge products deposition (Figure 3B). Moreover, the morphology and chemical composition of discharge product is also highly dependent on the surface area as well as pore size of the carbon cathode, which is determined by the discharge reaction kinetics of Na-O$_2$ batteries (Figure 3C,D). The importance of carbon cathode properties in determining the discharge capacity and cycle life of Na-O$_2$ cell performance was also highlighted by Bender et al.[30] Discharge capacities of Na-O$_2$ batteries with different types of carbon cathode varied from 300 to 4000 mAh g^{-1} under the same experimental conditions, although pure NaO$_2$ cubes were identified as the discharge product in all cells. The difference in capacity can be attributed to the microstructure of the cathode, which can greatly affect the size and morphology of the NaO$_2$ products, with insufficient pore size leading to less efficient use of pore volume. More recently, to maximize the potential of
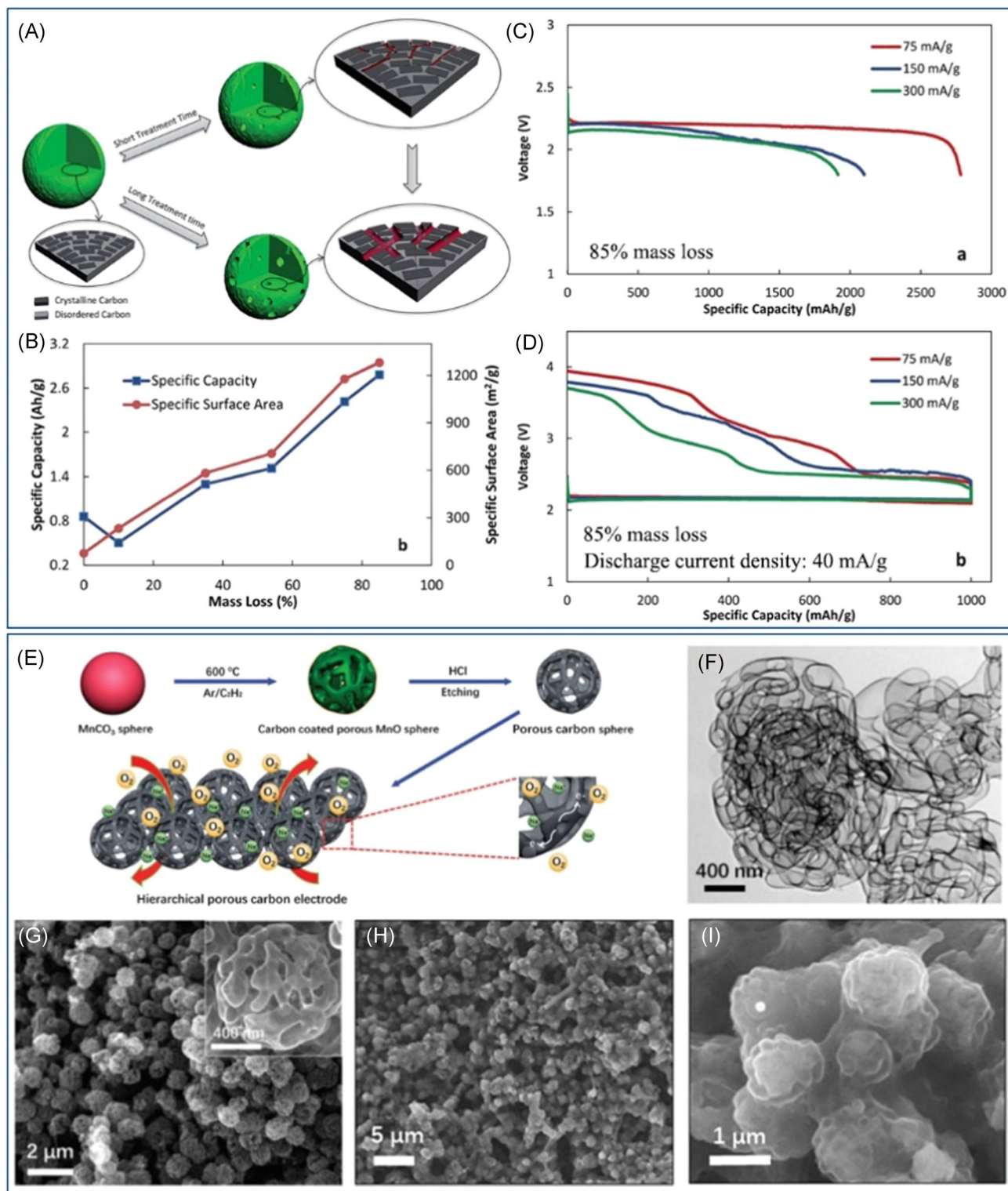
FIGURE 3 A, Schematic diagram of the carbon black electrode material during the heat-treatment process; (B) plot of specific capacities and specific surface area of the cathode materials of the cells as a function of mass loss; (C, D) Discharge/charge curves of Na-air cell using NH_3-treated carbon materials with 85% mass loss as the cathode at different current densities (Reproduced with permission from Reference,[56] Copyright 2014, Royal Society of Chemistry); (E) schematic illustration of the synthesis processes for PCSs and a hierarchical porous oxygen cathode made from PCSs. The inset in (G) is a high magnification SEM image of PCSs. F, Transmission electron microscopic and (G) SEM images of as-prepared PCSs. H and I, SEM images of discharged PCS electrodes at different magnifications (Reproduced with permission from Reference,[16] Copyright 2017, Wiley-VCH). PCS, porous carbon sphere; SEM, scanning electron microscope

the air electrode, Sun et al[16] prepared hierarchical porous carbon spheres (PCSs) through a facile chemical vapor deposition (CVD) method, and the typical transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images of PCSs are shown in Figure 3E-G.[16] The oxygen electrodes made of PCSs exhibited hierarchical porous structures that facilitated oxygen diffusion and electrolyte impregnation to the inner part of the air electrode, contributing to the high capacity and rate capability of Na-O$_2$ batteries. More importantly, the discharge product, NaO$_2$, showed a film-like morphology, which can be easily decomposed in comparison with microsized NaO$_2$ cubes (Figure 3H,I).

One-dimensional materials such as carbon nanotubes (CNTs) have also been employed as the oxygen diffusion electrode in Na-O$_2$ batteries due to the high void volume between 1D structures. A vertically aligned carbon nanotubes (VACNTs) electrode was reported by Zhao et al[57] (Figure 4). Benefiting from the reversible formation and decomposition of NaO$_2$, which can be electrochemically decomposed with a low overpotential (~0.2 V), the energy efficiency of Na-O$_2$ cell with VACNTs electrodes is as high as 90%. Further, a high discharge capacity of 4200 mAh g^{-1} was delivered at 67 mA g^{-1} and 130 cycles can be achieved with a limited capacity of 750 mAh g^{-1}, which could be attributed to the high surface area and the interconnected, well-developed pore structure of the VACNTs electrodes. While it is also

noteworthy that the optimal atmospheric conditions (static Ar/O$_2$ [80/20 vol%]) also contributed to the good cell performance by suppressing the side reactions involving trace H$_2$O. In another study, Jian et al[58] used a floating catalyst CVD method to prepare CNT paper that composed of interpenetrating CNTs. The resultant CNT paper was directly employed as the air electrode without adding any binders and additives, and a high initial discharge capacity of 7530 mAh g^{-1} was delivered at 500 mA g^{-1}. The main crystalline discharge product of constructed Na-O$_2$ cell is identified to be Na$_2$O$_2$·2H$_2$O through X-ray diffraction characterization.

As a typical two-dimensional material, graphene has also attracted substantial attention in energy-storage research.[59] Liu et al,[60] for the first time, employed graphene nanosheets (GNSs) in Na-O$_2$ batteries in 2013. Na-O$_2$ cell with a GNS electrode showed an excellent electrochemical performance with a high discharge capacity of 9268 mAh g^{-1}, which is superior to the 2030 mAh g^{-1} of normal carbon film cathode at the same current density of 300 mA g^{-1}. Although Na$_2$O$_2$ rather than NaO$_2$ was identified as the discharge product due to the electrolyte composition, oxygen partial pressure, and air electrode properties, GNS demonstrated its enormous potential in the application in Na-O$_2$ batteries. Graphene possesses high surface area and sufficient active sites, which is beneficial for the ORR process of Na-O$_2$ batteries. However, the GNS tend to restack due to van
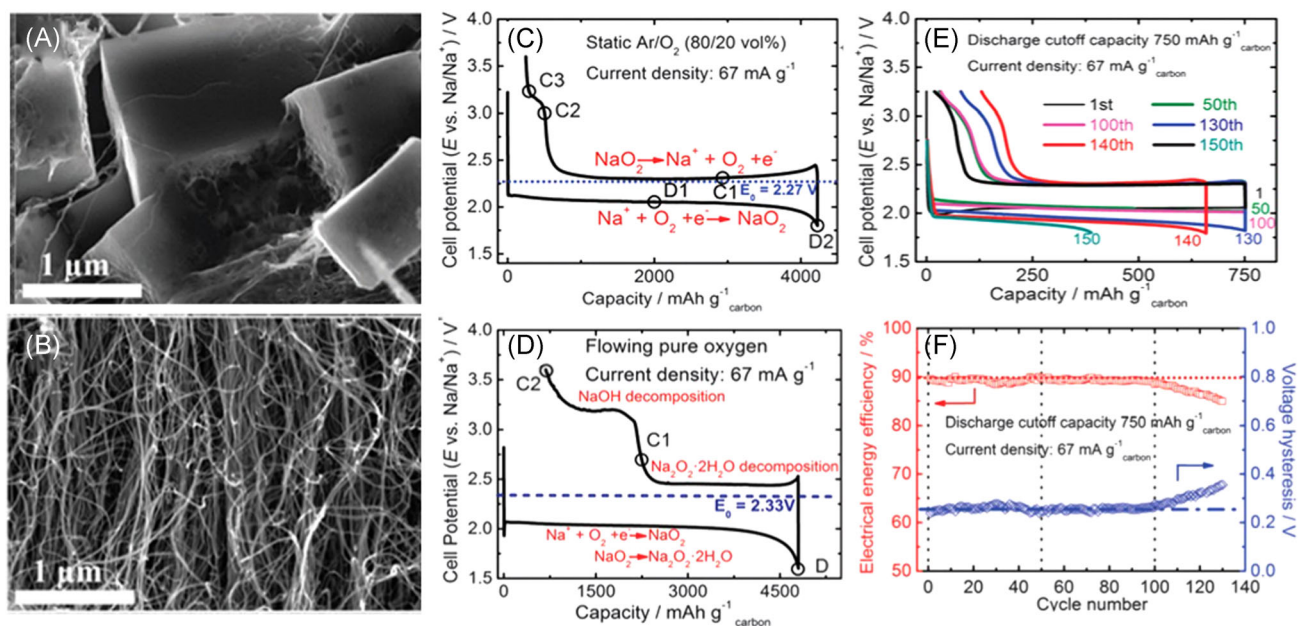

FIGURE 4 Scanning electron microscopic images for the VACNT cathodes disassembled from the Na-O$_2$ batteries operated under the static Ar/O$_2$ (80/20 vol%) atmosphere at different electrochemical stages: (A) complete discharge to 1.8 V, (B) recharge to 3.25 V. The typical discharge/charge profiles of Na-O$_2$ cells with VACNT cathodes operated in (C) static Ar/O$_2$ (80/20 vol%) and (D) flowing pure O$_2$ at 67 mA g$_{carbon}$$^{-1}$. E, Cycling performance of Na-O$_2$ batteries in the static Ar/O$_2$ (80/20 vol%) atmosphere and (F) corresponding electrical energy efficiency and voltage hysteresis (Reproduced with permission from Reference,[57] Copyright 2014, Royal Society of Chemistry). VACNT, vertically aligned carbon nanotube

der Waals or capillary forces, which would decrease the active area and limit the effective diffusion of O_2 within the graphene-based cathodes.[61] By controlling the freezing temperature of reduced graphene aerogels, reduced graphene oxide (rGO) air electrodes with different porosities were successfully developed by Vitoriano and co-workers.[62] They found that air electrode porosity plays a key role in battery capacity and cyclability by influencing the oxygen supply. Due to the sufficient oxygen diffusion and ORR/OER reaction kinetics, graphene-based electrodes with meso-macroporosity and a narrow macropore size arrangement exhibit the best performance among all cathodes (6.61 mAh cm^{-2}). This study further indicates that tuning of material porosity is an effective strategy to facilitate the oxygen diffusion and eliminate the diffusional/kinetic limitations toward ORR and OER in Na-O_2 batteries, especially at high rates.

Three-dimensional carbon paper (CP, H2315) gas diffusion layer, which possesses pores on the scale of dozens of micrometers, is another good candidate for the air electrode in Na-O_2 batteries. CP as the air electrode in Na-O_2 batteries was first reported by Hartmann et al[14] in 2013. A high initial discharge capacity of 3.3 mAh was delivered at 120 μA cm^{-2}, much higher than that of the Li-O_2 cell counterpart using the same cathode (Figure 5A). More importantly, the charge overpotential of Na-O_2 batteries is significantly lower than that of Li-O_2 batteries, as shown in Figure 5B. These results indicate the distinct reaction mechanisms between Li-O_2 and Na-O_2 battery systems, and the reversible formation/decomposition of NaO_2 cubes via one-electron transfer in Na-O_2 batteries is verified (Figure 5C,D). Moving forward, CP has been widely used as the air electrode to investigate the cell electrochemistry, as well as the physicochemical factors affecting the electrochemical behavior of Na-O_2 batteries.[15,23,35,38,63,64] Note that both current density and O_2 pressure have a large effect on the spatial deposition of NaO_2 through CP cathode, and the maximum capacity is limited by insufficient O_2 supply as a result of CP cathode pore clogging at low current densities and high O_2 pressure (Figure 5E).[63-65] Therefore, to alleviate the pore-clogging effect and enable continuous O_2 diffusion, air electrodes with decoupled oxygen and electrolyte pathways can be developed in future studies.[66,67]

3.2 | Heteroatoms-doped carbon materials

The microstructure of the air electrode is critical as the overall cell capacity and energy density are highly dependent on the amount of insoluble discharge products that can be accommodated within the porous electrode structure. It should be noted that the chemical properties of

the air electrode also plays an important role in affecting the discharge/charge behavior and thus determining the overall cell performance, especially for the peroxide-based Na-O_2 batteries.[26] To tackle the sluggish electrochemical oxidation kinetics of peroxide-based products, air electrode optimization is essential for Na-O_2 batteries. Doping foreign atoms, such as N, S, O, and P into the carbon cathode structure is an effective strategy to tailor the electronic structure, chemical nature, as well as the electrocatalytic activity of the electrode.[68,69] Moreover, the heteroatom-doped catalytic sites are at the atomic level, which contribute to a high catalytic site density on the electrode at a low doping quantity. Heteroatom-doped carbon materials have widely reported as the air electrode in Li-O_2 batteries and supercapacitors.[70-74] Due to their excellent electrocatalytic activity toward ORR and OER reaction kinetics, heteroatom-doped carbon materials have also been reported as an effective air electrode in Na-O_2 battery system.

As a typical example, N-doped graphene nanosheets (N-GNSs) were fabricated and used as the cathode material in sodium-air batteries by our group in 2013.[51] We found that the N-GNSs demonstrated significantly improved electrocatalytic activity toward ORR, and the discharge capacity of GNSs is two times higher than that of the pristine counterpart (Figure 6A). The electrochemical enhancement can be related to the charge delocalization in the GNSs structure due to the N-doping, resulting in a high positive charge density of the neighboring carbon. The charged carbon can act as the active sites with a strong O_2 adsorption to facilitate the uniform nucleation of discharge products during discharge (Figure 6B,C). This is consistent with the theoretical calculation of the catalytic role of the defective site in graphene, which indicated the effectiveness of N-doping to facilitate nucleation of Li_2O_2 cluster in Li-O_2 batteries.[75] Self-stacked N-doped CNT (NCNT) as air electrode for Na-O_2 batteries have been investigated by Sun et al,[53] which exhibited higher rate performance and extended cycle life at high current densities in comparison with CNT electrode. The outstanding catalytic activity of the N-doped sites in NCNT contributed to high cycling stability of the cell. It should also be noted that the enhanced electrochemical performance can be attributed to the robust network of aligned NCNTs, which enabled rapid oxygen and Na$^+$ transport while accommodating the discharged product. In another research study, Zhang et al prepared N-doped carbon materials with two different doping methods.[76] They found that using N-containing precursor to prepare the target materials can give a different pore distribution with increased surface area, and at the same time, maintain considerable N content, which is more desired compared with the ammonia activation method. In
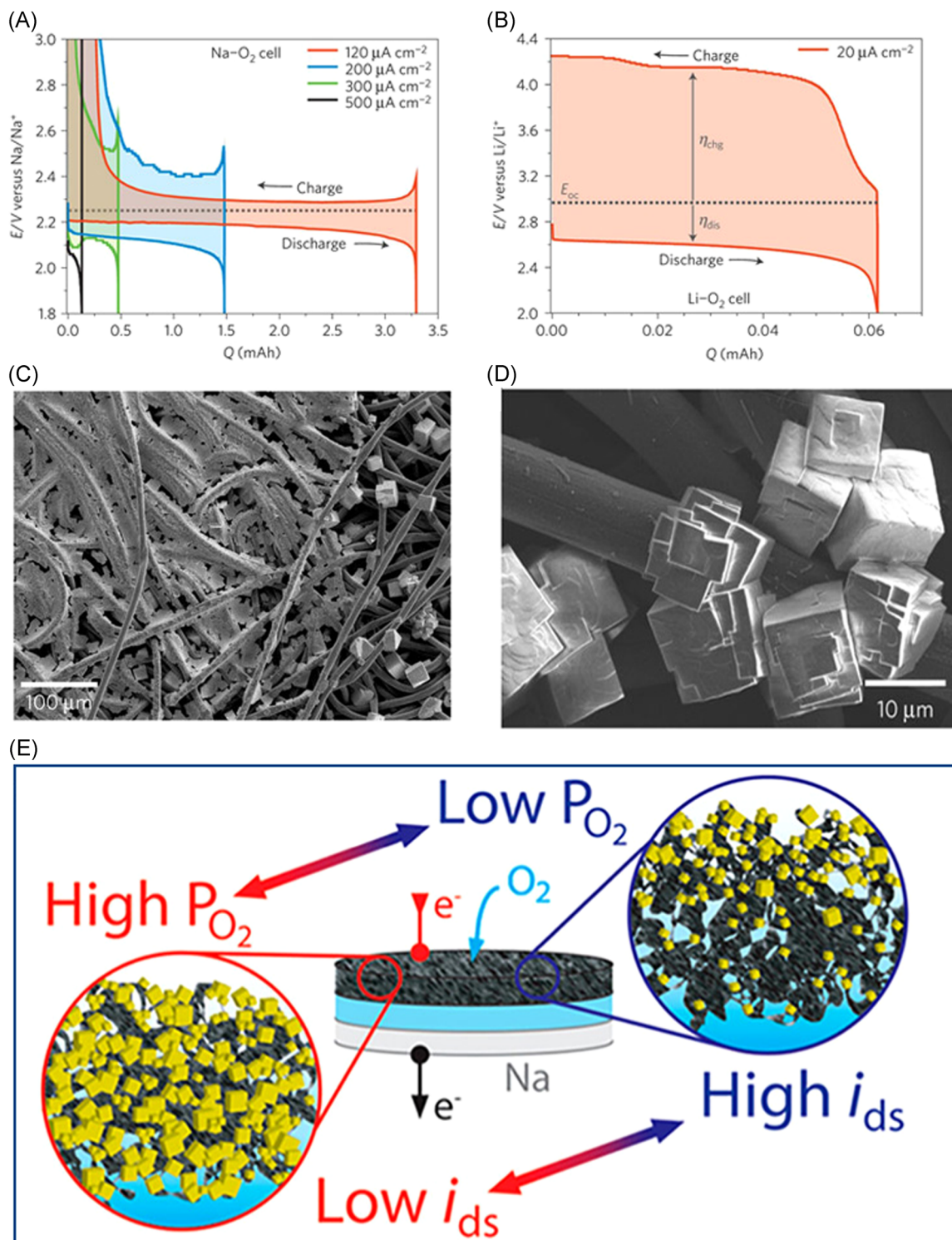
FIGURE 5 A, Discharge-charge cycles of Na-O$_2$ cells with GDL cathodes at various current densities, (B) discharge-charge voltage profile of a Li-O$_2$ cell with GDL cathode for comparison. C and D, scanning electron microscopic images of GDL cathode after discharge to 2 mAh at 80 µA cm^{-2} (Reproduced with permission from Reference,[14] Copyright 2013, Nature Publishing Group). E, Schematic illustration of the effect of current density and oxygen pressure on the spatial deposition of NaO$_2$ through the cathode (Reproduced with permission from Reference,[63] Copyright 2018, American Chemical Society). GDL, gas diffusion layer

addition, the importance of treatment temperature on the pore structure, N content of air electrode, as well as the electrochemical performance of Na-O$_2$ batteries was also verified.

A free-standing air electrode composed of N-doped graphene aerogels on Ni foam (3D N-GA) was success-fully synthesized by Zhang et al[78] using a one-step hydrothermal method. Due to the unique properties of
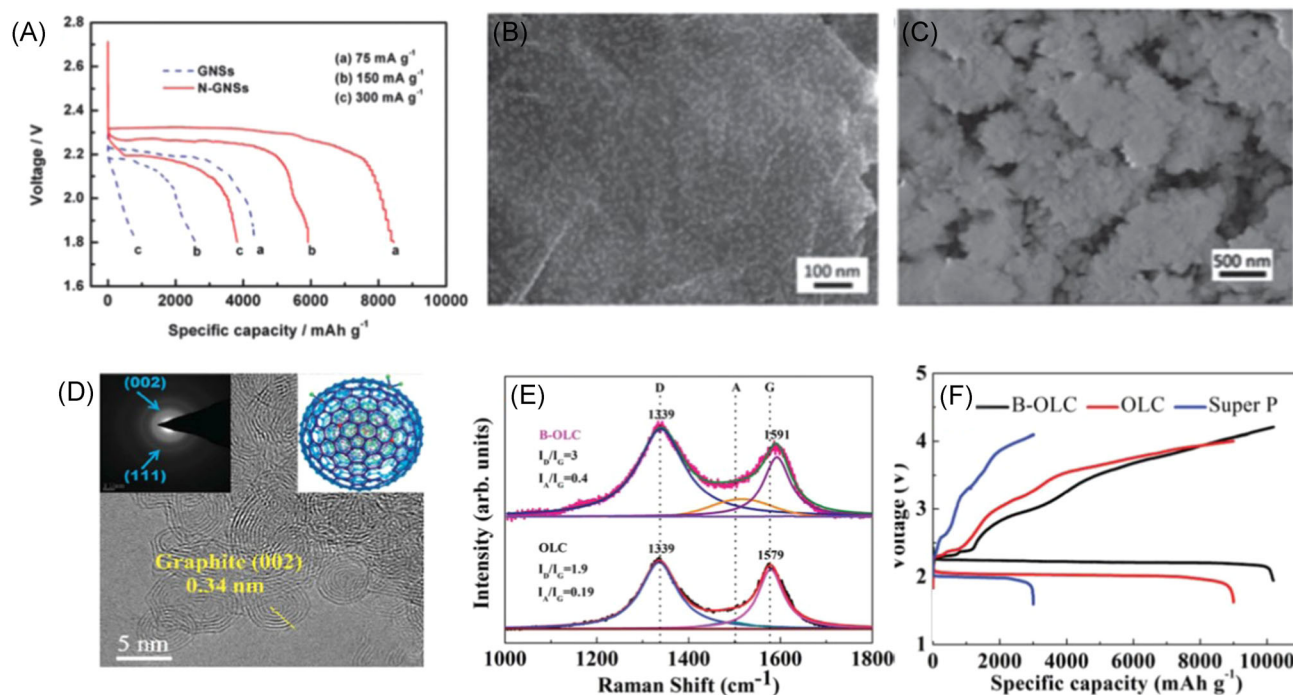
FIGURE 6 A, The discharge curves of GNS and N-GNS electrodes, scanning electron microscopic images of N-GNS electrodes after (B) discharged for 12 hours and (C) fully discharged (Reproduced with permission from Reference,[77] Copyright 2013, Royal Society of Chemistry). D, High-resolution transmission electron microscopic image and selected area electron diffraction pattern (inset) of B-OLC, (E) Raman spectra of B-OLC and OLC, (F) discharge/charge curves of B-OLC, OLC, and Super P electrodes in Na-O_2 batteries at a current density of 0.15 mA cm^{-2} (Reproduced with permission from Reference,[52] Copyright 2016, Royal Society of Chemistry). B-OLC, boron-doped onion-like carbon; GNS, graphene nanosheet; N-GNS, N-doped graphene nanosheet

interconnected architecture with excellent conductivity, high surface area, and ideal pore size distribution, Na-O_2 batteries with 3D N-GAs@Ni air electrode delivered a high discharge capacity of 10 950 mAh g^{-1} at a current density of 100 mA g^{-1} while only 9230 mAh g^{-1} can be achieved for GAs@Ni at the same current density. By further investigating the morphology of the discharged air electrode, they revealed that the N-doping of graphene also plays an important role in facilitating the uniform deposition of Na_2O_2 discharge product at the nanoscale, as well as the reduction of Na_2O_2 with lower overpotential. It should be noted that other than an interconnected porous architecture and positive effect of N-doping, the binder-free property of 3D N-GAs@Ni also contributed to the good performance of Na-O_2 cell by avoiding the side reactions involving polymeric binders. For the same purpose, 3D nanostructured air electrode composed of vertically grown N-doped CNT on CP (NCNT-CP) was developed and used as the air electrode for Na-O_2 batteries.[18] The NCNT-CP synthesized by CVD method could deliver a high discharge capacity of over 11 mAh cm^{-2}, which is about 17 times higher than that of bare CP at 0.1 mA cm^{-2}. The increase in discharge capacity is related to the increased surface area due to the introduction of NCNT on CP skeleton, as well as the

continuous O_2 and Na$^+$ transportation through the micrometer pores of the CP structure. Similar to N-doped graphene, the N-doped CNT also shows advantages in tuning the discharge product morphology and enhancing cycle life compared with pure CNT.[53] By using synchrotron-based X-ray absorption spectroscopy, the electrochemical and chemical mechanism of the Na-O_2 cell with NCNT-CP cathode was further investigated. NaO_2 and NaO_2 are identified as the main discharge products of the cell; while the formation of carbonate-based side product and its gradual accumulation on the air electrode surface restrict the cycle life, it should not be ignored in future studies.

Other than N-doping, theoretical and experimental studies showed that incorporating boron atoms into the carbon lattice also can be a good catalytic substrate that facilitates the oxidation of peroxide discharge products.[73,79] As reported by Shu et al,[52] the boron-doped onion-like carbon (B-OLC) was synthesized by a simple thermal method and then applied as the cathode for nonaqueous Na-O_2 batteries (Figure 6D-F). Similar to N-doped carbon, adsorption of O_2 on B-doped carbon is easier due to the distinct electronegativity between oxygen and boron, which is prerequisite for the subsequent reaction. The resulting B-OLC cathodes

exhibit outstanding electrochemical performance with high specific capacity (10 200 mAh g^{-1}), good rate capability, and cycling stability, which is superior to that of Super P and OLC electrodes. The improvement of cell performance could be reasonably ascribed to the synergistic effect of unique porous structure of B-OLC and its improved catalytic activity after boron doping.

Previous reports indicated that Na-O$_2$ battery with N- or B-doped carbon cathode exhibit higher capacity, lower overpotential, and longer cycle life compared with pristine counterpart. Additionally, N and S co-doped graphene has shown superior ORR performance comparable with that of commercial Pt/C catalyst, and the ORR activity was much better than the graphene solely doped with S atoms or N atoms due to their synergistic positive effect.[80] To further improve the conductivity and catalytic activity of N-doped carbon fiber (NCF), Zhang's group fabricated a free-standing NCF with in situ embedded and coated Co using a coaxial electrospinning technique (Co-ECNCFs).[81] By comparing the discharge-charge profiles of Na-O$_2$ cells with NCFs, Co-ECNCFs and Co-ECNCFs electrode with etched off accessible Co nanoparticles (Co-ECNCFs-A), they found that the Co-ECNCFs cathode exhibit the lowest charge overpotential, highest discharge capacity, and longest cycle life. Other than the unique structural properties of Co-ECNCFs and fast electron/mass transport within the electrode, the synergy between N-doping and Co encapsulation/coating plays an important role in tailoring the discharge product morphology, as well as the significantly improved ORR/OER kinetics.

3.3 | Carbon as support/host materials for catalysts

Apart from the heteroatom-doped carbon cathodes discussed in the previous section, metals and/or metal oxides have also been used as the catalyst to decrease the charge overpotential and enhance the overall performance of (peroxide-based) Na-O$_2$ batteries. The reported metal and/or metal oxide as catalysts mainly including noble metal and/or their oxides, transitional metal and/or their oxides, perovskite-related oxides and their combinations. Considering that solid-state catalysts are metal-based and possess relatively high density, which will cause the compromise on the key advantages of cathode in high capacity and energy density, anchoring the nanometer- or micrometer-sized solid catalysts onto the porous carbon framework may simultaneously enhance the reaction kinetics and increase the specific energy of the battery. In this section, we will summarize the recent progress in fabricating highly efficient air electrodes that incorporate carbon materials with solid catalysts to address the sluggish kinetics of peroxide oxidation in Na-O$_2$ batteries.

GNS loaded with homogeneous dispersed Pt nanoparticles (Pt@GNS) was successfully developed by Yang and co-workers via a hydrothermal method.[82] The presence of Pt nanoparticles not only acts as additional oxygen adsorption sites that benefits the capacity increase, but also prevent discharge product aggregation by regulating the uniform deposition of discharge products. Consequently, significantly improved capacity and cycling stability were achieved, as well as enhanced ORR and OER kinetics under the shallow cycling mode. The Ag nanoparticle decorated rGO (Ag-rGO) as a bifunctional oxygen electrode for ORR and OER was investigated by Kumar and co-workers. However, different to the formation of Na$_2$CO$_3$ on the discharged Pt@GNS electrode, NaO$_2$, Na$_2$O$_2$, and Na$_2$O were identified as the discharge products in cells assembled with Ag-rGO.[83] More recently, the electrochemical behavior of Au-coated CP cathode was investigated by Grimaud and co-workers. Distinct to the traditional formation of micrometer-sized NaO$_2$ cubes on CP surface, the strong affinity of Au with O$_2$/O$_2^-$ on Au-coated CP cathode results in the formation of NaO$_2$ thin flakes with decreased capacity.[36] Pd nanoparticles as the catalysts for the cathode was reported by Amine et al recently, and a peroxide-based Na-O$_2$ battery with low overpotential and high discharge capacity was successfully developed.[26] Kang et al[84] used ruthenium-decorated CNTs (CNT/Ru) as the solid catalyst to enhance the ORR and OER kinetics of Na-O$_2$ batteries, and high energy efficiency can be achieved due to the formation of deficient sodium peroxide (Na$_{2-x}$O$_2$) as a main discharge product.

In fact, the composition and morphology of the discharge products are mainly determined by the surface chemistry and microstructure of the air electrode. In a recent research work, Ren and co-workers found that the characteristics of the air electrode plays an important role in determining the discharge/charge behaviors, nature of the discharge products, and accordingly Na-O$_2$ cell performance, as depicted in Figure 7.[85] Micrometer-sized NaO$_2$ and nanosized film-like NaO$_2$ are the main discharge products of rGO and B-doped rGO cathodes, respectively. With further decoration of micrometer-sized RuO$_2$ on the surface of B-rGO (m-RuO$_2$-B-rGO), nanosized spherical amorphous Na-deficient Na$_{2-x}$O$_2$ was formed due to the high affinity of RuO$_2$ for oxygen. More importantly, the amorphous Na$_{2-x}$O$_2$ phase in discharged m-RuO$_2$-B-rGO cathode has good electrical contact with the RuO$_2$ particles, and thus can be decomposed completely under 3.1 V, contributing to a significant enhancement of cycle life compared with other cathodes.

Besides noble metals, transition metal-based materials (eg, oxide) are also reported as catalysts for Li/Na-O$_2$ batteries, which demonstrated promising activity toward ORR and/or OER.[86-88] More recently, transition metal-based catalysts have aroused great interest to enhance the catalytic
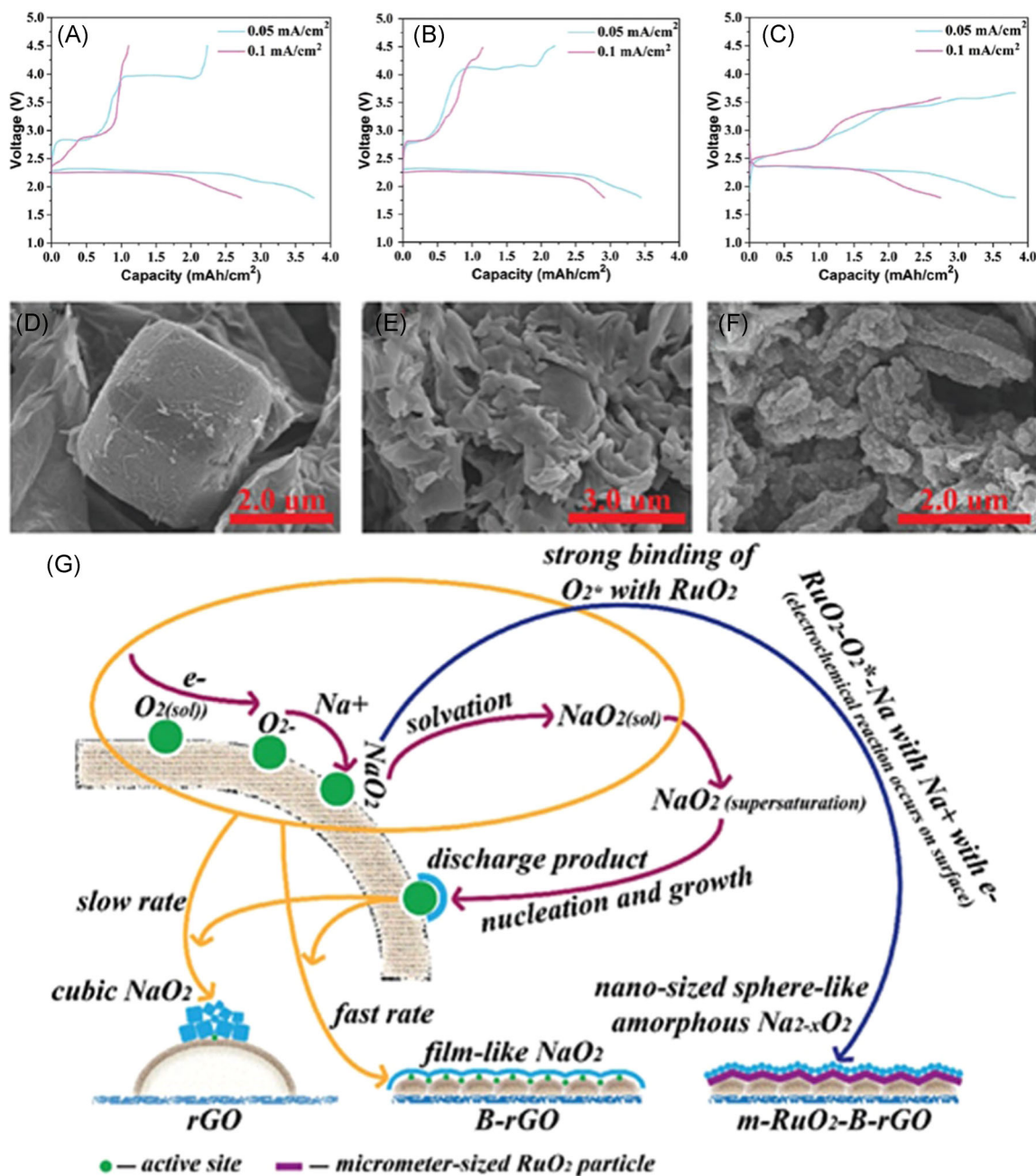
FIGURE 7 Deep discharge/charge curves of Na-O$_2$ batteries with (A) rGO, (B) B-rGO, (C) m-RuO$_2$-B-rGO cathodes at 0.05 and 0.1 mA cm^{-2} in the voltage range of 1.8 to 4.5 V vs Na$^+$/Na, scanning electron microscopic images of discharged (D) rGO, (E) B-rGO, and (F) m-RuO$_2$-B-rGO cathodes at 0.05 mA cm^{-2}. G, Schematic illustration of the proposed mechanism accounting for the different morphology of discharge products on different electrodes (Reproduced with permission from Reference,[85] Copyright 2017, Wiley-VCH). rGO, reduced graphene oxide

activity of cathode in Na-O$_2$ battery system. For example, our group synthesized Co$_3$O$_4$-decorated CNTs (CNT@Co$_3$O$_4$) via atomic layer deposition (ALD), and then employed as the cathode catalysts for Na-O$_2$ batteries (Figure 8A,B).[50] Synchrotron-based X-ray analysis revealed that the well-dispersed Co$_3$O$_4$ catalyst on CNTs could serve as functionalized active sites and promote the electrochemical decomposition of sodium peroxide, superoxide, and carbonates. High-spin Co$_3$O$_4$ as the electrocatalyst for Na-O$_2$ batteries

was reported by Mai and co-workers. The growth of NaO$_2$ nanowires induced by high-spin Co$_3$O$_4$ catalyst significantly boosts the electrochemical performance of Na-O$_2$ batteries (Figure 8C,D).[89] In another work, free-standing C@NiCo$_2$O$_4$ air electrode composed of vertical NiCo$_2$O$_4$ nanoneedle arrays on CP has been delicately fabricated by Liu et al[90] through a hydrothermal method. The porous CP skeleton enables fast electron transport and oxygen diffusion, while the NiCo$_2$O$_4$ nanoneedles provide adequate active sites and
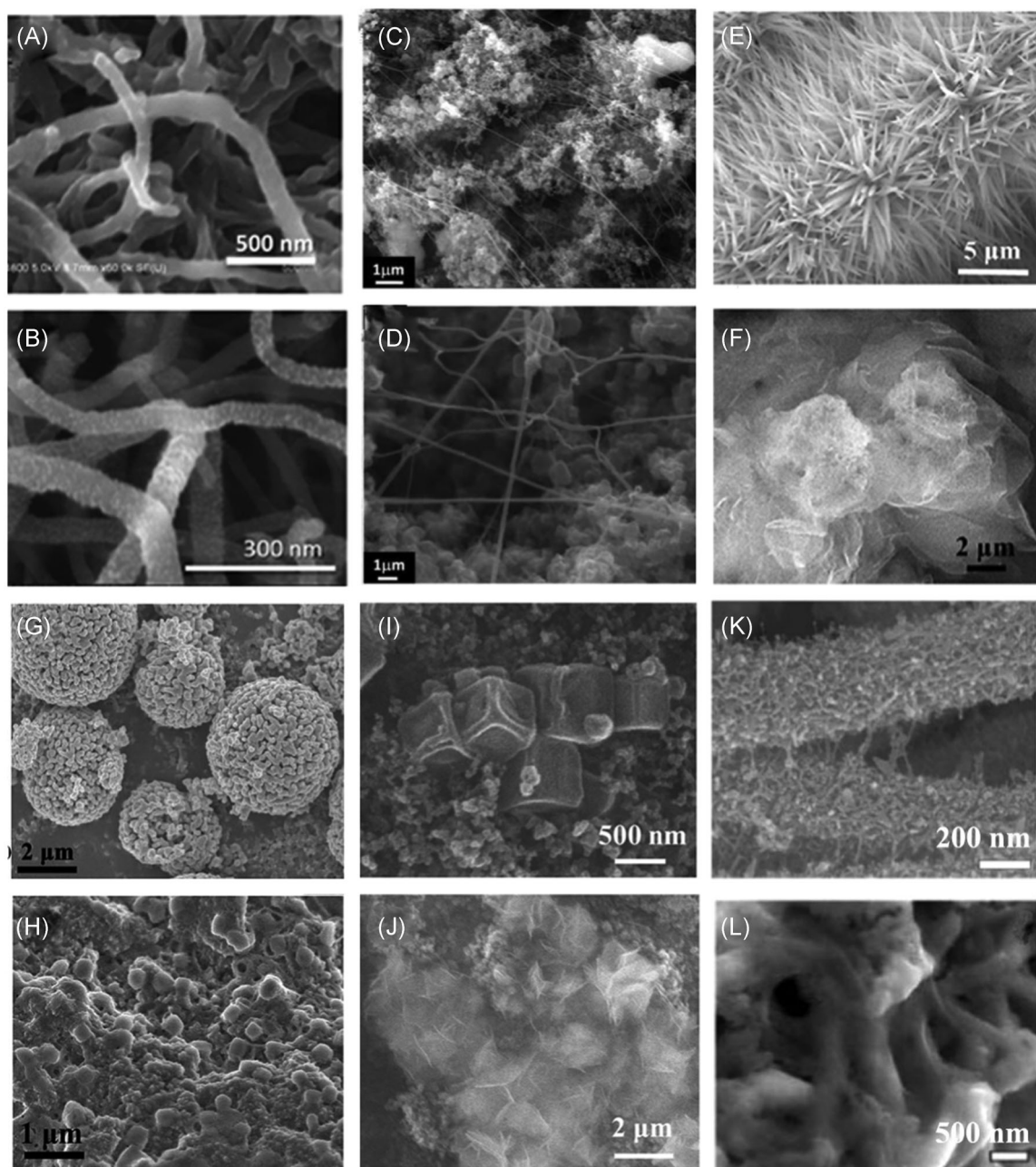
FIGURE 8 SEM images of (A) pristine and (B) discharged ALD CNT@Co$_3$O$_4$ electrode at 300 mA g^{-1} (Reproduced with permission from Reference,[50] Copyright 2017, Wiley-VCH). C and D, SEM images of NaO$_2$ nanowires (discharge product of Na-O$_2$ batteries) beside the high-spin Co$_3$O$_4$ electrocatalyst (Reproduced with permission from Reference,[89] Copyright 2018, American Chemical Society). SEM images of (E) pristine and (F) discharged C@NiCo$_2$O$_4$-NAs electrode with a limited capacity of 6500 mAh g^{-1} (Reproduced with permission from Reference,[90] Copyright 2019, Elsevier). SEM images of (G) synthesized CaMnO$_3$ and (H) discharged CaMnO$_3$/C electrode (Reproduced with permission from Reference,[91] Copyright 2015, Royal Society of Chemistry). SEM images of (I) pristine and (J) discharged h-Co$_3$O$_4$@MnCo$_2$O$_{4.5}$ Ns electrode with a capacity limitation of 1000 mAh g^{-1} (Reproduced with permission from Reference,[92] Copyright 2019, Royal Society of Chemistry). SEM image of (K) pristine and (L) discharged RuO$_2$/Mn$_2$O$_3$/CNF electrode at 0.05 mA cm^{-2} (Reproduced with permission from Reference,[93] Copyright 2018, IOP Publishing). ALD, atomic layer deposition; CNT, carbon nanotube; SEM, scanning electron microscopy

sufficient space for discharged product accommodation (Figure 8E,F). Na-O$_2$ batteries with C@NiCo$_2$O$_4$ electrode delivered a discharge capacity of 6500 mAh g^{-1} with a low overpotential of 0.6 V at 50 mA g^{-1}. Moreover, over 120 cycles can be well maintained with a limited capacity of

800 mAh g^{-1} due to the reversible formation/decomposition of film-like Na$_2$O$_2$.

In addition to transitional metal oxide, several other metal-based catalysts have also been studied as cathode catalysts in Na-O$_2$ batteries and exhibited promising

catalytic activity toward both ORR and OER. For example, the introduction of CoB cathode catalyst successfully endowed Na-O_2 batteries with a low charge overpotential, good rate capability, and cycling stability benefiting from its high catalytic, electronic conductivity and unique porous structure.[94] Chen and co-workers reported the preparation of perovskite $CaMnO_3$ microsphere and its application as an efficient electrocatalyst for rechargeable Na-O_2 batteries (Figure 8G,H).[91] The micro-nanostructure of porous $CaMnO_3$ microspheres not only provides abundant active sites for bifunctional ORR/OER, but also provide adequate space for discharge product accommodation. Pyrochlore-type oxide as cathode catalyst have also been reported in Na-O_2 batteries.[95] Jiang et al found that the Na-O_2 cell performance is highly related to the electronic structure and specific surface area of pyrochlore-type oxide, and $La_2Co_2O_7$ catalyst enables a high-performance Na-O_2 battery with ultrahigh discharge capacity (20 184.2 mAh g^{-1}) and long cycle life (over 167 cycles).[95]

Owing to the limited catalytic activity of single-component oxide catalyst toward both ORR and OER, the design of efficient bifunctional electrocatalysts is highly desired. With this regards, Liu and colleagues constructed heterogeneously structured CoO/CoP nanosheets, which combine the advantages of the high OER activity of CoP and the high ORR activity of CoO.[96] More importantly, the catalytic activity of designed CoO/CoP nanosheets exceeds that of the parent CoO or CoP due to the interpenetration of O-P on the CoO/CoP interface. Hierarchical $Co_3O_4@MnCo_2O_{4.5}$ nanocubes (h-$Co_3O_4@MnCo_2O_{4.5}$ Ns) cathode catalyst with a yolk-shell structure was successfully fabricated by Liu et al[92] by using the metal-organic framework template (Figure 8I,J). In another work reported by Yilmaz and co-workers, 3D RuO_2/Mn_2O_3/CNF as bifunctional electrocatalysts toward ORR and OER were prepared, as shown in Figure 8K,L.[93] Taking the benefit of RuO_2 and Mn_2O_3 synergy, the RuO_2/Mn_2O_3/CNF electrode exhibits much higher specific capacity and catalytic activity compared with its CNF, Mn_2O_3/CNF, and RuO_2/CNF counterparts. The incorporation of heterogeneous catalysts to simultaneously boost the ORR and OER activity of Na-O_2 batteries was also reported by our group.[97] The NCNT@CP air electrode was decorated with mesoporous Mn_3O_4 as an ORR catalyst and ALD deposited Pd nanoclusters as OER catalysts. We found that the catalytic activity is related to the dynamic interaction between the catalyst and discharge products. Additionally, by monitoring the electronic state of the solid catalyst during ORR and OER, we further revealed that the synergistic effect between Mn_3O_4 and Pd catalyst originates from the electron exchange between the noble metal and the metal oxide.

Although the electrochemical performance and cycling life of Na-O_2 batteries have been improved, the research on the carbon-based air electrode in Na-O_2 batteries is still limited and the achievable electrochemical performance is still unsatisfied. Due to the similar working principles, the research results obtained from the Li-O_2 battery system may provide guidance for the future research of Na-O_2 batteries.

4 | CARBON-BASED MATERIALS FOR NA-O_2 BATTERY ANODE

Unlike the intense research on understanding the Na-O_2 cell electrochemistry and air electrode design, the study on the role of the anode in determining the overall cell performance has been less focused. In the Na-O_2 batteries, sodium metal foil is widely used as the anode material due to its high theoretical-specific capacity (1166 mAh g^{-1}) and low redox potential (-2.714 V vs standard hydrogen electrode). However, the Na dendrite growth and Na corrosion are identified as two major issues of Na-O_2 batteries, which severely degrades the cell-cycling performance. Among various strategies that can help achieve stable cycling of Na metal, rationally designed carbon materials have shown the greatest potential for large-scale fabrication and application in the Na metal protection. Therefore, this section summarizes the recent progresses using carbon-based materials to address the Na issues, and highlights the advantages and roles of carbon materials in Na protection for Na-O_2 batteries. Further, the potential carbon materials that can be used in protecting Na metal in the further study of Na-O_2 batteries are also discussed.

4.1 | Carbon-hosted sodium anode

In the Na-O_2 batteries, the Na dendrite growth has been identified as one of the main reason for the premature cell death, and is attracting much more attention recently.[47,98] Cell failure due to Na dendrite growth has also been studied in Na-ion batteries, and it is agreed that the Na dendrite growth is related to the properties of the SEI layer, the stability of the planar surface, and concentration profiles in the liquid electrolyte.[46] However, it is still unclear if the growth mechanism of Na dendrite in Na-O_2 batteries is identical to that of Na-ion battery system because of the distinct cell configuration, working principle, and operating environment, which needs further investigation.

So far, few studies have reported to restrain the dendrite growth and achieve long-term cycling of Na metal in Na-O_2 batteries. Achieving a robust SEI layer by

surface engineering is an effective strategy for the stabilization of Na metal in Na-O$_2$ batteries.[99] As reported by Zhou and co-workers, electrolyte additives (fluoroethylene carbonate) can be used to passivate the Na surface by forming a stable fluoride-rich film, which contribute to the dendrite-free anode and significantly improved cycling stability of Na-O$_2$ batteries.[48] There are also reports of protecting the Na surface by direct formation of an artificial protective layer via atomic/molecular layer deposition technique or solution-based method.[100-102] Designing of high-modulus separators/solid electrolytes have also shown to be effective in suppressing Na dendrite growth and alleviating Na degradation.[103] However, the electrolyte additives used for SEI stabilization are gradually drained during cell cycling, and the construction of an artificial protective layer is sophisticated and costly. Moreover, from the practical aspect, a thick and heavy membrane would drastically reduce the achievable energy density and may also reduce the power density of Na-O$_2$ batteries.

On the basis of the "Sand's time" theory and experimental result of Janek et al, current density has a determining effect on the morphology of Na deposits.[46,104] By significantly reducing the local current density with 3D electrode, the growth of Na dendrite growth can be effectively restrained. Among various 3D current collectors to facilitate uniform Na$^+$ flux in Na batteries, 3D carbon frameworks have shown the greatest potential for large-scale fabrication and application in the future due to its unique properties[105-108]: (a) carbon materials with high surface area and porosity can construct 3D host or interlayer for Na metal, which can lower the local current density for uniform Na deposition. At the same time, the infinite volume expansion of Na metal during continuous stripping/platting also can be well-addressed; (b) the "Na-philic" functional groups/nanomaterials on the carbon surface help increase sodium affinity, which facilitate homogeneous Na nucleation with a low overpotential; (c) carbon films with high mechanical flexibility and chemical stability can act as a protective layer for stabilizing the SEI layer, which not only suppress the Na dendrite, but also alleviate the Na corrosion; (d) carbon materials are relatively light and cost effective, and at the same time, the thickness and porosity of the 3D carbon networks can be easily controlled. Although the study on suppressing the Na dendrite growth and Na degradation with carbon-based materials is relatively scarce in Na-O$_2$ batteries, the earlier research toward Na protection in symmetric cells provides some guidance for the rational design of carbon materials for stabilizing Na metal anode in Na-O$_2$ batteries.[45]

Rational design of 3D carbon hosting for metallic Na is an effective strategy to alleviate the dendrite growth by decreasing the electrode current density. In designing Na

metal anode for Na-O$_2$ batteries, the 3D carbon host should be prestored with Na to supply the Na source. Compared with electrodeposition, which is complex and time consuming, thermal infusion strategy with molten Na infused into a 3D sodiophilic carbon substrate is much more promising. Luo and colleagues used rGO as a host to fabricate a processable and moldable composite Na metal anode (Na@rGO) for Na batteries, as shown in Figure 9A.[109] Interestingly, by controlling the thickness of the densely stacked GO film, the Na@rGO anode thickness can be determined, which was found to be 20 times the thickness of the GO film. Moreover, the shape of Na@rGO composite anode can also be engineered by tailoring the precursor GO films with desired shapes. With only 4.5 wt% of GO, the mechanical properties and corrosion stability of Na@rGO composite anode significantly improved while not sacrificing much capacity of Na anode. Consequently, the dendrite-free Na anode with enhanced cycling performance can be achieved in Na symmetric cells using both ether and carbonate electrolytes. As a proof of concept, the electrochemical performance of Na-O$_2$ cells using Na@rGO anode was further investigated, which exhibits a lower discharge/charge overpotential and improved cycling stability compared with that of the cell with bare Na anode.

In another work reported by Hu et al, carbonized wood with channels was used as a 3D host for fabricating Na-wood composite anode with thermal infusion process (Figure 9B).[110] The hierarchical structure of carbonized wood can be well maintained after encapsulation of metallic Na, which offers a large surface area for homogeneous Na deposition by lowering the effective current density. Benefiting from its unique structure, the Na-wood composite electrode exhibited stable cycling performance for over 250 cycles at 1 mA cm^{-2} with a capacity of 0.5 and 1.0 mA cm^{-2}, respectively, while the cell with bare Na electrode only run for less than 90 cycles and 50 cycles under the same testing conditions. Recently, the rational design of Na@CP-NCNT composite electrode with 3D CP-NCNT framework host was reported by Sun and co-workers, and schematic presentation of electrode fabrication process is shown in Figure 9C.[111] Interestingly, the cross-conductive network of CP and NCNT can facilitate the uniform Na deposition by decreasing the local current density. However, the "Na-phobic" property of CP changes to "Na-philic" after introducing NCNT on the CP skeleton. More importantly, the constructed Na@CP-NCNTs composite electrode exhibited improved cycling stability compared with bare Na electrode at high current densities of 3 and 5 mA cm^{-2}. Even at high 5 mA cm^{-2} with a high capacity limit of 3 mAh cm^{-2}, the Na@CP-NCNTs electrode also can stably run for over 90 hours. Although the electrochemical performance of Na@CP-NCNTs electrode did not characterize in the
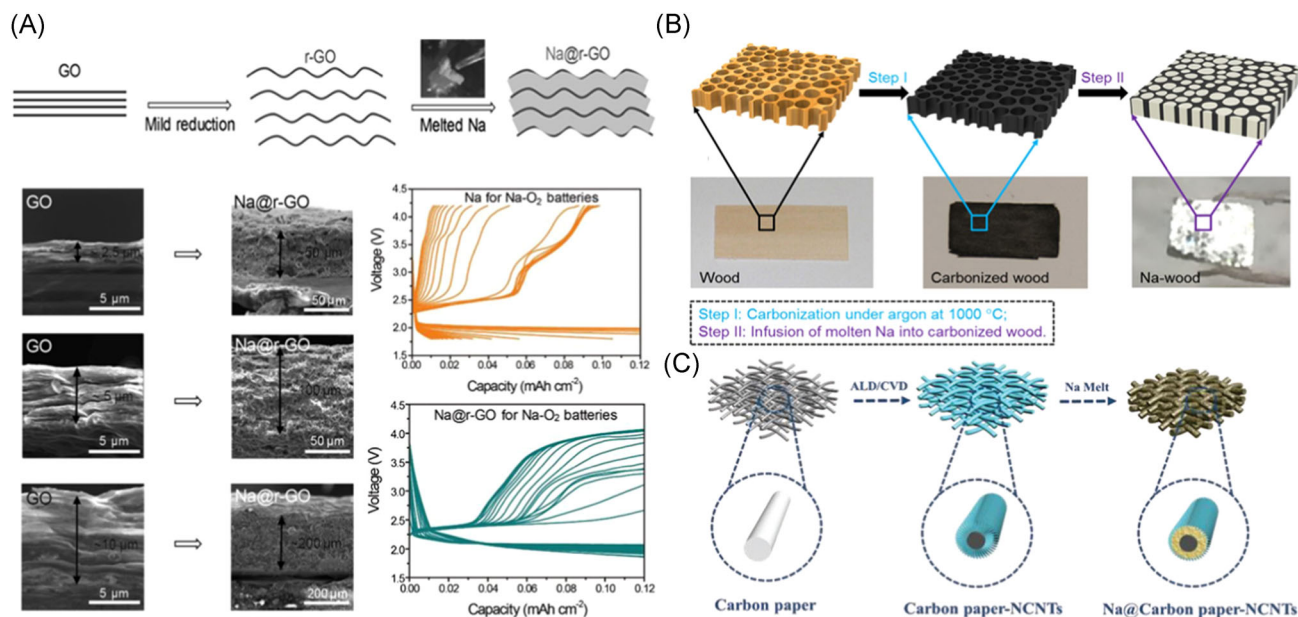
FIGURE 9 A, Schematic representation of the preparation of Na@r-GO composites, and the cycling performance of Na-O$_2$ batteries with Na and Na@r-GO anode from the 1st and 20th cycle (Reproduced with permission from Reference,[109] Copyright 2017, Wiley-VCH). B, Encapsulation of metallic Na into carbonized wood by a spontaneous and instantaneous infusion (Reproduced with permission from Reference,[110] Copyright 2017, American Chemical Society). C, Schematic diagram of the fabrication procedure of Na@CP-NCNTs (Reproduced with permission from Reference,[111] Copyright 2018, Wiley-VCH). ALD, atomic layer deposition; CVD, chemical vapor deposition; NCNT, N-doped carbon nanotube; r-GO, reduced graphene oxide

Na-O$_2$ batteries, the design of 3D host with "Na-philic" property provides some guidance in fabricating advanced Na anode in the future study of Na-O$_2$ batteries.

Aside from pre-store the Na metal into 3D host to stabilize the Na anode by decreasing the local current density, significantly improved cycling performance of Na anode was also demonstrated by introducing commercial CP as an interlayer between Na metal and separator.[112] The positive effect of CP was attributed to its high surface area for decreasing current density. More importantly, this method is straightforward, cost effective, and time saving, which is beneficial for the practical application of Na metal batteries. However, uniform deposition of Na metal is hardly achieved at high current density with a high Na capacity. Decorating the carbon materials with functional groups is an effective strategy to increase the affinity of substrate for sodium, as reported by Wang and colleagues, who introduced a nitrogen and sulfur co-doped CNT (NSCNT) interlayer on the Na metal anode in Na-O$_2$ batteries (Figure 10A).[22] The N- and S-containing functional groups on the CNT induce the NSCNT to be "sodiophilic," which can regulate the initial Na nucleation and enable uniform deposition of Na on the interlayer. The large surface area and good electronic conductivity of NSCNT are also beneficial for dendrite-free Na anode even at a high current density. More than Na ions regulation, porous NSCNT structure can buffer the infinite volume change

of Na during continuous platting/stripping process. Consequently, the assembled Na-O$_2$ battery using Na/NSCNT anode shows very stable cycling performance for over 90 cycles, while the cycling of Na-O$_2$ cell using bare Na anode was interrupted by short-circuiting at the 53rd cycle due to the Na dendrite penetration.

It is worth noting that the Na deposition also can be regulated through heterogeneous nucleation seeds other than functional groups/defects. In the research of Na metal anode, Yang and colleagues investigated the nucleation behavior of sodium on different metals.[113] They found that the Na can be controllably deposited onto the main group II metal substrates such as Be, Mg, and Ba as they have definite solubility in sodium. The formation of solid solution surface layer enables guidance on the Na growth in the parallel direction of metal substrates, as well as significantly reduced Na nucleation barrier. Another impressive work has been reported by Tang and co-workers, they introduced a layer of Au to realize stable Na deposition by alloying. With the formation of a "sodiophilic" Au-Na alloy layer on Cu substrate, the Na could be uniformly deposited with low overpotential.[114] As 3D carbon framework are effective in suppressing the Na dendrite and infinite volume expansion, heterogeneous nucleation seeds are beneficial for regulating Na deposition and realizing spatial control over Na nucleation. It is expected that homogeneously dispersing sodiophilic nanoseeds onto the skeleton of 3D
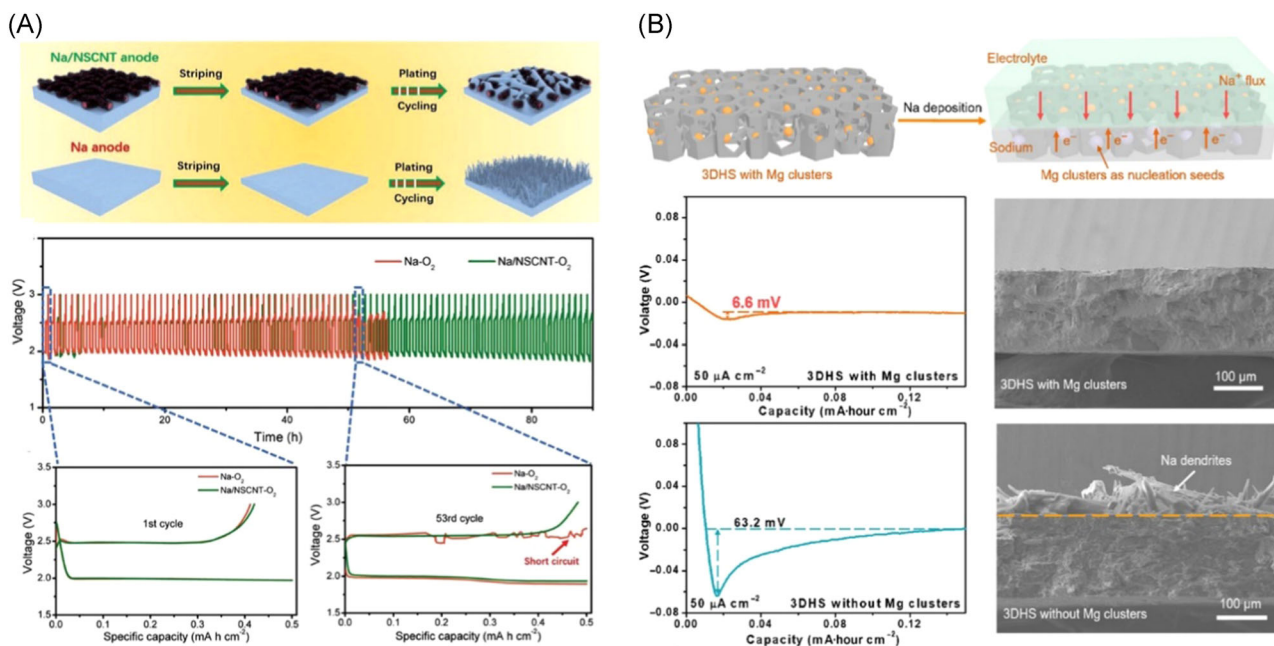
FIGURE 10 A, Schematic illustration of the metallic Na striping/plating on Na metal anode and Na/NSCNT anode, and the cycling performance of Na-O_2 batteries with Na anodes and Na/NSCNT anodes at 1 mA cm^{-2} with a cut-off capacity of 0.5 mA cm^{-2} (Reproduced with permission from Reference,[22] Copyright 2018, Wiley-VCH). B, Controllable nucleation and growth of Na in the 3DHS film with Mg clusters at 50 μA cm^{-2} (Reproduced with permission from Reference,[113] Copyright 2019, American Association for the Advancement of Science). NSCNT, nitrogen and sulfur co-doped carbon nanotube

carbon-based substrates can direct the deposition of Na within the 3D structure, resolving the issues of Na dendrite growth in Na-O_2 batteries (Figure 10C). Furthermore, the difference in the Na nucleation barrier between different materials suggest an effective way to construct sodiophilic-sodiophobic gradient interlayer, which can alleviate the preferential nucleation of Na on the top surface of conductive interlayer at high current density,[115] ensuring long-term cycling of dendrite-free Na anode in high energy density Na-O_2 batteries.

4.2 | Carbon-based material as anode protection layer

Considerable efforts have been made to demonstrate the feasibility of using carbon materials to suppress the dendrite growth as mentioned above. In fact, modification of the Na metal anode with a carbon-based protective layer also shows great potentials in alleviating Na corrosion in Na-O_2 batteries. In our recent work, a Na-O_2 battery using electrically connected CP with Na metal as a protected anode is successfully developed.[23] Interestingly, we found that the function of CP is beyond that of a conductive 3D current collector to prevent the Na dendrite growth; the CP also acts as a protective layer to alleviate the Na degradation during cycling. More specifically, the electrochemical potential of the CP gains a pseudo-equal potential when in contact with Na metal, and the side reactions induced by O_2/O_2^-

crossover preferentially occur on the CP instead of Na surface (Figure 11A). Consequently, the cycling stability of constructed Na-O_2 batteries can be significantly improved compared with that of the cell using bare Na anode. Though this strategy has been demonstrated to be effective in alleviating Na degradation, it cannot fully inhibit the contaminants' crossover in the long-term cycling process due to its highly porous structure, which provide abundant contaminants' diffusion paths.

In fact, different to mitigating the Na dendrite growth by introducing 3D carbon-based current collector/composite electrode, carbon films with a relatively dense structure are more desired to alleviate the Na corrosion in Na-O_2 batteries. Free-standing graphene films have been reported as an artificial protection layer on Na metal surface to stabilize the SEI layer as well as physically blocking the Na dendrite growth, which makes it ideal for suppressing side reactions induced by contaminants crossover on the Na metal surface (Figure 11B).[116] On one hand, the contaminants only can diffuse through the interlayer ionic channels of the graphene layers rather than migrate freely from the cathode to the Na metal surface. On the other hand, the high surface area of graphene layer is hardly covered by the side products, ensuring a significantly improved cycle life of Na metal anode in the presence of contaminants' crossover. A similar strategy has been reported in Li-S batteries, and an integrated anode composed of a compacted graphite film and Li metal was developed by Huang et al.[118] Lithiated
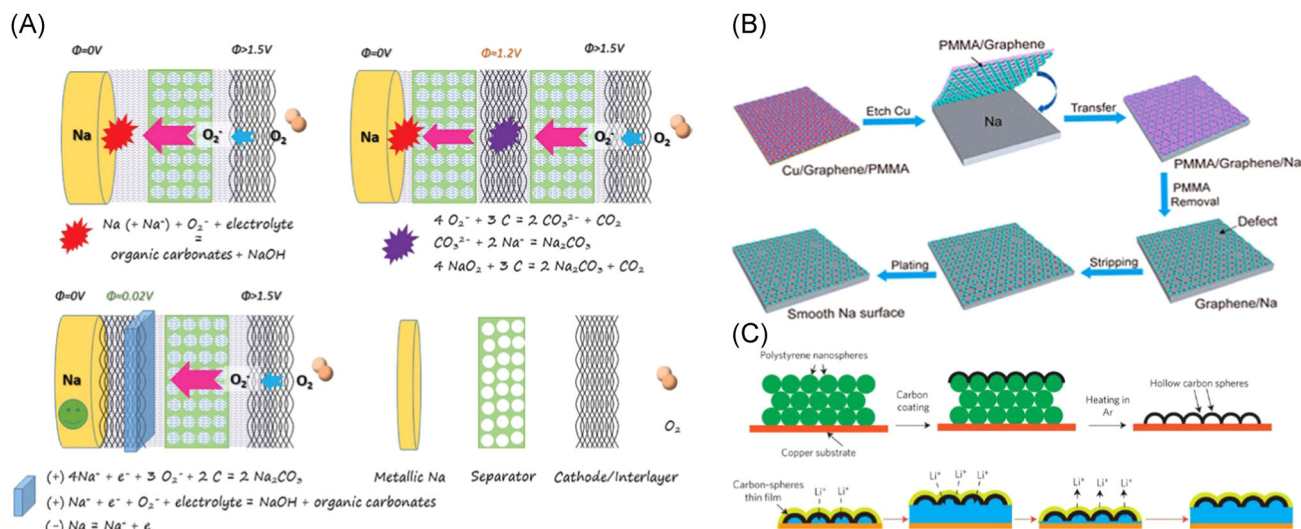
FIGURE 11 A, Illustration of the protective effect of CP interlayer toward Na corrosion induced by superoxide radical crossover (Reproduced with permission from Reference,[23] Copyright 2018, Wiley-VCH). B, Illustration of preparation and stripping/platting behavior of graphene-coated Na anode (Reproduced with permission from Reference,[116] Copyright 2017, American Chemical Society). C, Fabrication process for the hollow carbon nanosphere-modified Cu electrode, and modifying the Cu substrate with a hollow carbon nanosphere layer creates a scaffold for stabilizing the SEI layer (Reproduced with permission from Reference,[117] Copyright 2014, Nature Publishing Group). CP, carbon paper; PMMA, poly(methyl methacrylate); SEI, solid-electrolyte interphase

graphite placed in front of the Li metal not only can effectively stabilize the SEI layer on Li surface, but also simultaneously retard the etching of Li metal by migrated polysulfides, realizing dendrite-free Li anode and enhanced cycling performance of the Li-S batteries. Amorphous carbon also has the potential to be used as a protective layer on Na metal anode. A monolayer of interconnected amorphous hollow carbon spheres coating as a stable interfacial layer on Li metal was developed by Cui and colleagues (Figure 11C).[117] Due to the conductivity difference between carbon sphere and current collector, Li metal deposition takes place on the Cu current collector and a stable, conformal SEI layer forms on the carbon nanospheres. The SEI layer formed on the interconnected carbon surface is not only effective in inhibiting dendrite Li growth, but also can help prevent the penetration of solvent molecules and contaminants, which shows great feasibility in preventing Na degradation Na-O$_2$ battery system.

As discussed above, developing protective carbon layer coating on Na metal anode is an effective strategy to alleviate the Na corrosion caused by contaminants' crossover, at the same time, such carbon layer also acts as a 3D current collector or physical barrier to suppress the dendrite growth. More importantly, fabricating a protective layer on the Na metal anode is a universal and effective approach to effectively restrict the O$_2$/O$_2^-$ reaching the Na surface, and it can be expected that the longer cycle life of Na-O$_2$ batteries can be achieved using a more effective protective layer on Na metal anode.

4.3 | Sodiated carbon as the anode material

The Na dendrite growth and corrosive oxidation due to the high reactivity of metallic Na cause critical problems for safety, reversibility, and cycling stability of Na-O$_2$ batteries. In principle, the negative effect of issues related to Na metal anode can be circumvented by replacing Na metal with a sodium alloy/compound or Na-ion intercalation materials. For example, to prevent the undesired reaction between Na metal and dimethyl sulfoxide-based electrolyte, presodiated antimony, Na-Sb alloy, was adopted as an anode material in Na-O$_2$ batteries by Dilimon et al.[119] Li-Na alloy as anode material has also been studied, and a novel bimetallic Li-Na alloy-O$_2$ battery was successfully developed.[120] However, the dendrite growth and huge volume expansion of Li-Na anode during repeated cycling still restrict the long-term cycling of the electrode, and thus electrolyte additives were adopted to achieve Li-Na alloy-O$_2$ battery with significantly improved cycling stability.

Carbon-based Na insertion materials, which show relatively small volume expansion by sodiation, appear to be one of the most promising candidates for Na-O$_2$ batteries anode material due to its unique physical and chemical properties.[121] As expected, pioneering research work using sodiated carbon anode in a Na-O$_2$ battery has been reported by Janek and colleagues.[122] The CP was first sodiated in a coin cell with a Na metal foil as a counter electrode. Then, a Na-O$_2$ full cell was assembled with sodiated carbon as a

replacement for Na metal anode. In this case, the parasitic reactions related to Na metal anode can be significantly reduced during cycling. In addition, the sodiated carbon anode does not participate in redox reactions and only acts as the supporting material for reversible Na^+ intercalation in this study. Thus, the safety issues caused by dendrite growth as a result of nonuniform deposition of Na^+ on Na metal surface during long-term cycling also can be avoided. Although replacing Na metal with sodiated carbon significantly undermines the achievable capacities, the sodiated carbon performs well as anode as the safety and cycling stability of the constructed $Na-O_2$ cells significantly improved. In addition, lower crystalline carbons, such as soft and hard carbons, show higher electrochemical activity in sodium cells, and thus higher specific capacities may be achieved by future $Na-O_2$ batteries using carbon-based anode with a disordered structure.

5 | CONCLUSION AND PERSPECTIVE

Nonaqueous $Na-O_2$ batteries have attracted enormous attention during the last decades owing to their high energy density, low cost, and environmental friendliness. As discussed above, much effort has been made in exploring the cell chemistry and incorporating various carbon-based materials into $Na-O_2$ batteries to improve its electrochemical performance. Figure 12 schematically summaries the rationally designed carbon materials in $Na-O_2$ batteries. Although significant progress has been achieved in designing advanced carbon-based cathode and carbon-protected Na anode, $Na-O_2$ battery technology is still at an immature stage and many challenges still remain in making this promising energy-storage system practically applicable.

Electrochemistry of the $Na-O_2$ battery is still elusive and controversial. The slight difference in the experimental parameters, such as the microstructure and surface chemistry of air electrodes, the composition and concentration of organic electrolyte, as well as the atmospheric conditions, would affect the nature of discharge products and thus the battery performance. A fundamental understanding of the working mechanism and impact factors is crucial for the development of high-performance $Na-O_2$ batteries. Theoretical calculation and various in situ/in-operando characterization may help in searching for the underlying mechanism of this system.

As a key component in $Na-O_2$ battery, the development of highly efficient carbon-based cathodes has been of interest due to its crucial role in determining the overall cell performance. As discussed, rational structure design through tailoring porous structure can effectively increase the specific capacity and cycle life of the batteries. However,
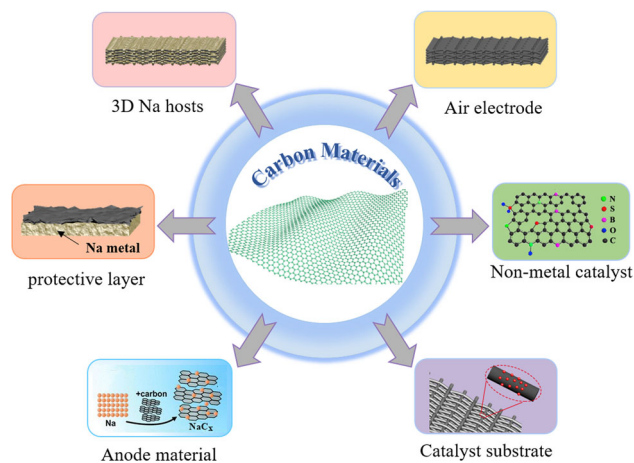

FIGURE 12 Schematic summaries of rationally designed carbon materials for high-performance $Na-O_2$ batteries (Reproduced with permission from Reference,[122] Copyright 2015, Royal Society of Chemistry)

carbonaceous cathode corrosion is still one of the major problems that hinders the cell performance. It is worth noting that protection strategies such as surface coating can help boost the chemical stability of carbon cathode. With the rapid development of nanotechnology, uniform surface coating with a high conductivity, high stability, and low-cost material on the carbon electrode surface can be expected in the near future. In addition to surface coating, introducing a solid catalyst is another effective strategy to alleviate carbon cathode corrosion by decreasing the charge potentials. As the carbon decomposition occurs at high charge potential, the attachment of catalyst on carbon cathode can facilitate peroxide oxidation with a lower charge overpotential, and thus the side reactions involving carbonaceous cathode can be wisely avoided. However, it should be noted that, to screen a suitable catalyst in $Na-O_2$ batteries, we should not only focus on the effectiveness of catalyst in facilitating peroxide decomposition, the parasitic reactions promoted by the catalysts should also not be neglected. Additionally, to mitigate the side reactions induced by polymer binder's decomposition, binder-free air electrode design is more desired to improve the stability of $Na-O_2$ batteries.

In fact, the most outstanding advantage of $Na-O_2$ batteries comes from its high theoretical energy density, which is a result of high capacity of not only cathode materials but also sodium metal. Although the safety issues caused by Na dendrite growth, as well as the Na degradation induced by O_2/O_2^- crossover severely limit the cycling stability of Na metal carbon materials have been proved to be effective to promote the practical application of Na metal and $Na-O_2$ batteries due to their multifunctional roles, such as acting as a stable Na host, lowering the local current density, stabilizing the SEI layer, and blocking the contaminants crossover.

However, the research on Na protection in Na-O$_2$ battery system has been severely overlooked, and designing ideal carbon materials for Na protection and practical use in Na-O$_2$ batteries are urgently needed. It is also necessary to understand the mechanism underlying the Na dendrite growth in Na-O$_2$ batteries, and the optimization of the organic electrolyte to constructive robust and stable SEI layer on the Na metal should also be considered.

Apart from fabricating advanced air electrode and protected anode by carefully controlling the properties of carbon materials, modification of the battery separator with carbon materials can also act as a physical O$_2$/O$_2^-$ crossover trap to avoid the detrimental side reactions on Na metal surface. Additionally, chemical impediment toward O$_2^-$ crossover also can be expected by introducing functionalized carbon layer, which may be capable of anchoring the polarized O$_2^-$ on the surface of carbon interlayer surface, and avoid its further migration toward Na surface. One thing which should be noted is that unlike direct placement of the carbon film between separator and cathode in Li-S batteries, the carbon interlayer should be sandwiched between two layers of the separators in the Na-O$_2$ battery system.

So far, the Na-O$_2$ batteries are still in its initial stage of development, further enhancement of the cell performance still needs technology breakthrough in mechanism study and electrode designing. As Na-O$_2$ and Li-O$_2$ battery system exhibit similar working principles, previous research on Li-O$_2$ battery systems would be helpful for providing guidance for the future research direction of Na-O$_2$ batteries. We believe that, with more and more efforts being devoted, the practical application of Na-O$_2$ batteries can be expected in the future.

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