

## RECHARGEABLE NA-O<sub>2</sub> AND NA-CO<sub>2</sub> BATTERY RESEARCH: CURRENT STATUS AND PROSPECTS

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### Abstract:

*Research into rechargeable sodium–oxygen (Na-O<sub>2</sub>) and sodium–carbon dioxide (Na-CO<sub>2</sub>) batteries has been increasing in recent years because of its advantages, such as high theoretical energy density and low cost, as well as the availability of sodium resources. There are still many hurdles to overcome in the early stages of the development of Na-O<sub>2</sub> and Na-CO<sub>2</sub> batteries, such as poor energy efficiency and short cycle life. Because of this, knowing their working principles and the chemical and electrochemical processes of the electrodes is essential to their practical use and even the objective of real sodium–air batteries." Accordingly, this study focuses on a wide range of topics, including working processes, air cathode materials, sodium anode protection and electrolyte stability in Na-O<sub>2</sub> and Na-CO<sub>2</sub> battery research. In addition, the remaining concerns and future research prospects are extensively examined and presented.*

### 1. Introduction

Modern society's reliance on fossil fuels might lead to even higher greenhouse gas emissions in the atmosphere. [1,2] In 2060, carbon dioxide emissions are expected to total 496 gigatonnes, [3] which might lead to an even greater degree of global warming and climate disruption. As a consequence, in order to minimise our dependency on fossil fuels and alleviate the intractable issue of the greenhouse effect, we must create renewable and clean energy technology. As a result of their renewable resources, renewable forms of energy such as solar, wind, tidal, and hydroelectric power are attractive. [4,5] For this reason, secondary batteries, fuel cells and supercapacitors are needed to store their extra energy. [6] Secondary batteries, particularly rechargeable lithium-ion batteries (LIBs), have received the most attention because of their superior benefits, such as high energy density, minimal maintenance, low self-discharge, and extended cycle life, among others. [7,8] Portable electronic gadgets like smartphones, laptops, tablets, and digital cameras have all benefited greatly from LIBs' dominance in the power supply industry since their introduction in 1991. [9–11] In spite of this, its theoretical specific energy density limit of 350–400 Wh kg<sup>-1</sup> does not match the needs of future applications that require greater gravimetric and volumetric energy densities, such as long-distance electric cars and large-scale energy storage systems. Metal–sulfur and metal–air batteries, among other energy storage devices, have been suggested to break this constrained state of affairs and replace present LIB technologies for such purposes. [12,13] It is common for high-energy metal–air batteries to be comprised of cathodes made of porous electrodes, ion conducting separators, and anodes made of alkali or alkaline earth metals with sufficient gas diffusion paths. [14,15] Renewed interest in next-generation energy storage devices has focused on rechargeable Li-air and Na-air batteries because of their superior high theoretical energy density and their reliance on natural gases. [16–18] This is because CO<sub>2</sub> and H<sub>2</sub>O in the ambient environment would interfere with the chemical pathway and create side reactions, which would make the batteries less efficient. [19] The Li-O<sub>2</sub> battery, initially published in 1996, has been the most widely investigated metal–air battery in recent decades.

In comparison to commercial LIBs, which use continuous insertion and extraction of Li ions between graphite and LiCoO<sub>2</sub> (387 Wh kg<sup>-1</sup>), the theoretical specific energy of Li-O<sub>2</sub> batteries might supply 3502 Wh kg<sup>-1</sup> (based on 2Li<sup>+</sup> + O<sub>2</sub> + 2e<sup>-</sup> → Li<sub>2</sub>O<sub>2</sub>). [21–24] Although Li-O<sub>2</sub> batteries have a lot of promise, they are hampered by a number of difficult challenges, such as slow oxygen redox kinetics and well-known concerns with reversibility and cyclability. [25–28] This overpotential would lead to low round trip efficiency and unstable cycling. Liquid resources are further constrained by their high cost and unequal distribution, which will further limit their future use. For these reasons, sodium-air batteries are a more economical and environmentally friendly option due to the abundant and inexpensive sodium supplies. [29] Na-air batteries, like their Li-ion siblings, can only be used in a pure oxygen environment. There have been many attempts to produce a Li-O<sub>2</sub> battery alternative, including Peled et al.'s [30] Na-O<sub>2</sub> battery, which was successfully demonstrated in 2010 at 105°C. [31] The first rechargeable Na-O<sub>2</sub> battery that could be used at room temperature was built by Sun et al. [32]. The chemical processes of rechargeable Na-O<sub>2</sub> batteries are distinct from those of Li O<sub>2</sub> batteries, according to subsequent studies. Discharging rechargeable Na-O<sub>2</sub> batteries in a dry nonaqueous electrolyte and an ultrahigh-purity oxygen atmosphere results in the formation of the discharge product NaO<sub>2</sub>, that is, 2NaO<sub>2</sub> = Na + 2O<sub>2</sub>.

As a result of the ensuing charge process, the NaO<sub>2</sub> decomposes and releases oxygen, reducing the Na<sup>+</sup> ion to Na and forming sodium anode plates on the cathode side. [32,33] The theoretical energy density of Na O<sub>2</sub> batteries is determined to be 1108 Wh kg<sup>-1</sup> based on the NaO<sub>2</sub> discharge product. [34] It is possible that Na-O<sub>2</sub> batteries might have a significantly lower charging overpotential than lithium-ion batteries because of the reversible electrochemistry of the O<sub>2</sub>=O<sub>2</sub><sup>-</sup> redox pair. [35,36] Other than that, the most difficult problem for Na-O<sub>2</sub> batteries is that the formation of Na<sub>2</sub>O<sub>2</sub> during the discharge process would compete with that of NaO<sub>2</sub>, since peroxide formation is thermodynamically favoured (E<sup>0</sup> (Na<sub>2</sub>O<sub>2</sub>) = 2.33 V, E<sup>0</sup> (NaO<sub>2</sub>) = 2.27 V), [32] where E<sup>0</sup> is the standard electrode potential, while charging overpotential with Na<sub>2</sub>O<sub>2</sub> as discharge product is not superior to that of Li-O<sub>2</sub> batteries. Understanding the operating mechanism of Na-O<sub>2</sub> batteries, managing the composition of discharge products, and achieving minimal charging overpotential are all critical. Additional air gas components including N<sub>2</sub>, CO<sub>2</sub>, and moisture must also be considered in the development of viable Na-air batteries for future applications.

The adverse effects of N<sub>2</sub> may be avoided since N<sub>2</sub> does not react with Na metal under cell conditions. Poor cyclability and excessive polarisation may be caused by water molecules reacting with both the Na anode and the discharge products. Fortunately, dry air may alleviate this problem without the presence of water. Because organic electrolytes, such as Na-air batteries, often employ CO<sub>2</sub>, as a non-negligible component, it must be introduced and researched. [37] In addition, Na<sub>2</sub>CO<sub>3</sub> has a greater Gibbs free energy of formation than NaO<sub>2</sub> (905.6 kJ/mol), which implies that the stability of Na<sub>2</sub>CO<sub>3</sub> is significantly higher than that of NaO<sub>2</sub> and that there is a propensity to produce more stable Na<sub>2</sub>CO<sub>3</sub> in Na-air batteries in the presence of CO<sub>2</sub>. This necessitates doing research on the Na-CO<sub>2</sub> batteries, which might also offer a unique way for the collection and conversion of CO<sub>2</sub> into electricity. [39] Using a combination of CO<sub>2</sub> and O<sub>2</sub> as the air cathode was originally reported in 2012 by Das et al. [40] for the first time in a nonaqueous Na-O<sub>2</sub> battery with CO<sub>2</sub> help. That CO<sub>2</sub> may be used as an active material in a Na-air battery has been shown. Using a multiwall carbon nanotube on Ni mesh as the cathode, Hu et al. [41] were able to get their batteries to run for 200 cycles in a pure CO<sub>2</sub> environment. A reversible reaction of 4Na + 3CO<sub>2</sub> → 2Na<sub>2</sub>CO<sub>3</sub> + C in a Na-CO<sub>2</sub> battery with the discharge product NaCO<sub>3</sub> delivered a theoretical specific energy of 1876 Wh kg<sup>-1</sup> at the time. The present research on Na-O<sub>2</sub> and Na-CO<sub>2</sub> batteries is still in its infancy, despite its appealing and exciting prospects of very high energy density for large-scale applications. Development of high-performance Na-O<sub>2</sub> and Na-CO<sub>2</sub> batteries is hampered by issues with the battery's primary components, such as the electrolyte, sodium anode, and the air cathode, including their poor energy efficiency and short cycle lives.

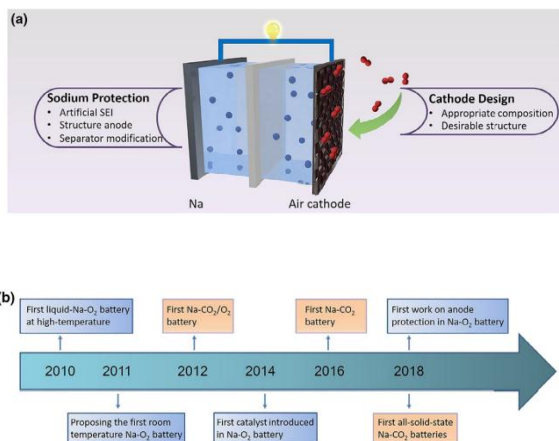
Consequently, these obstacles must be conquered and transformed into possibilities. First and foremost, the morphology and composition of discharge products in Na-O<sub>2</sub> batteries are determined by the use of appropriate materials and the structural design of oxygen cathodes. Electrolytes with chemical cyclability and an electrochemical window against superoxide radicals are also essential to prevent parasitic reactions of both the solvent and the electrolyte salts. Catalysts for improving the sluggish kinetics of CO<sub>2</sub> reduction and evolution processes should be developed for Na-CO<sub>2</sub> batteries in order to reduce polarisation and increase efficiency. The sodium anode in both Na-O<sub>2</sub> and Na-CO<sub>2</sub> batteries must be protected by reducing dendrite development and increasing tolerance to the dissolved gas and small quantities of moisture in the electrolyte. In this review, we'll cover everything you need to know about Na-O<sub>2</sub> and Na-CO<sub>2</sub> batteries in detail. Using air cathodes as an example, we'll begin by going through the electrochemical reaction processes. Research on air cathode design, electrolyte classifications and sodium anode protection are summarised in the next section. Lastly, the view and future research prospects include ways for increasing the performance of Na-O<sub>2</sub> and Na-CO<sub>2</sub> batteries to realise practical application of genuine Na-air batteries.

## 2. Reaction Mechanisms

Nonaqueous rechargeable Na-O<sub>2</sub> or Na CO<sub>2</sub> batteries are typically consisting of an air cathode, a sodium anode, and a separator with a suitable quantity of electrolyte (Figure 1a). Triple-phase zones are created by air cathodes, where molecule O<sub>2</sub> or CO<sub>2</sub> and sodium ions in the electrolyte (the liquid phase) are engaged in interfacial interactions with the discharge products and the air cathode, as well as the air cathode itself (the solid phase). Figure 1b shows the progression of work on the Na-O<sub>2</sub> and Na-CO<sub>2</sub> battery technologies throughout time. Na-O<sub>2</sub> and Na-CO<sub>2</sub> batteries need a thorough grasp of reaction processes in order to sensibly design system components. This part will thus go into the workings of Na-O<sub>2</sub> and Na-CO<sub>2</sub> batteries.

## Reaction mechanism of Na-O<sub>2</sub> batteries

Electrochemical processes in Na-O<sub>2</sub> batteries are comparable to those in Li-O<sub>2</sub> batteries in terms of dissolution/precipitation reactions. It is still unclear how Na-O<sub>2</sub> batteries respond, in contrast to LiO<sub>2</sub>, which has been universally acknowledged as the discharge product of Li O<sub>2</sub> batteries (even though LiO<sub>2</sub> has also been recorded in certain circumstances[42–44]). A number of distinct molecules, including NaO<sub>2</sub>, Na<sub>2</sub>O<sub>2</sub>, Na<sub>2</sub>O<sub>2</sub>·2H<sub>2</sub>O, and their mixes, have been found near the discharged cathode in various investigations to date. Then there were the diverse morphologies, including micrometer-scale cubic and nanorod forms of sodium oxalate, particles of sodium oxalate, and thin films of sodium oxalate·2H<sub>2</sub>O. There is no comprehensive explanation of how sodium oxides arise in Na-O<sub>2</sub> batteries, and it is unclear what variables could influence their composition and appearance. [53] A chemical reaction based on the fact that NaO<sub>2</sub> and Na<sub>2</sub>O<sub>2</sub> have been extensively reported as discharge products in the majority of investigations of Na-O<sub>2</sub> batteries has been proposed: NaO<sub>2</sub> is the cathode electrode! Anode electrode: Na!Na! (2) Cathode electrode: 2NaO<sub>2</sub>! NaO<sub>2</sub> (3) Nitrate of oxygen, or Na<sub>2</sub>O, is the anode electrode (5) An even lower Gibbs free energy is required at 298 K for the production of the Na<sub>2</sub>O<sub>2</sub> lattice than for the NaO<sub>2</sub> lattice with its higher Gibbs free energy. [54,55] Under typical circumstances, Na<sub>2</sub>O<sub>2</sub> is more thermodynamically stable than NaO<sub>2</sub>. Single-electron transfer to create NaO<sub>2</sub> is more favourable than the two-electron transfer process toward peroxide in terms of kinetic efficiency. [32] Even with a small free enthalpy difference of 12.2 kJ mol<sup>-1</sup>, it's difficult to tell which species is more thermodynamically stable under real-world cell circumstances. Furthermore, theoretical simulations show that the thermodynamic stability of sodium oxides may be affected by particle size because of the struggle between surface and bulk energy. [56] Under typical circumstances, bulk Na<sub>2</sub>O<sub>2</sub> is more stable than meta stable NaO<sub>2</sub>, according to the authors, and nanometer-scale NaO<sub>2</sub> is even more stable.



Rechargeable Na-O<sub>2</sub> and Na-CO<sub>2</sub> batteries are shown schematically in Figure 1a. Research on Na-O<sub>2</sub> and Na-CO<sub>2</sub> batteries has progressed rapidly in recent years.

liquid intermediate in the process. Nanosized NaO<sub>2</sub> is regenerated when it comes into contact with sodium, and the first nucleation of nanosized NaO<sub>2</sub> drives epitaxial growth to form micrometres of the material. An in-depth understanding of the reaction mechanism of Na-O<sub>2</sub> batteries at a carbon paper cathode was gained by Liu et al.[60] by the use of in situ X-ray diffraction. In Figure 2e, the diffraction peaks at 2  $\theta$  4.32°, 6.11°, and 7.16°, corresponding to (200), (220), and (331) reflections of NaO<sub>2</sub> (ICSD # 87176), reveal that NaO<sub>2</sub> formed during the discharge process. Furthermore, Lutz et al. found clear evidence of the creation of NaO<sub>2</sub> cubes by solution-mediated nucleation in another experiment. [61] When they used an operando electrochemical transmission electron microscopy, they observed that the development and dissolution of three-dimensional NaO<sub>2</sub> is caused by the solvation–desolvation equilibrium between NaO<sub>2</sub> (solv) and NaO<sub>2</sub> (solid) (TEM). For Na-CO<sub>2</sub> batteries, the reaction mechanism is 2.2 A byproduct of Na-CO<sub>2</sub> batteries discharging pure CO<sub>2</sub> has been found as Na<sub>2</sub>CO<sub>3</sub>. [41,62,63] Polycrystalline Na<sub>2</sub>CO<sub>3</sub> and amorphous carbon are formed when CO<sub>2</sub> molecules are reduced at the cathode and interact with sodium ions during the discharge process. In a reversible reaction, Na<sub>2</sub>CO<sub>3</sub> and amorphous carbon breakdown, and CO<sub>2</sub> is released in the following charge process. Using pure CO<sub>2</sub> as a cathode

gas, Hu et al.[41] built an in situ Raman battery capable of monitoring the discharge and charge processes in real time. The 1180 cm<sup>-1</sup> peak of stretching vibrational frequency was

given to Na<sub>2</sub>CO<sub>3</sub>, which emerged and grew throughout the charge process, then diminished and dissipated during the subsequent discharge. The C in Na<sub>2</sub>CO<sub>3</sub>'s carbonate radical was identified by XPS as the source of a new peak at 288.70 eV at the discharged cathode. Another way to confirm the carbon product's improved reversibility was by electron energy loss spectroscopy (EELS), which was performed using a transmission electron microscope (TEM). CO<sub>2</sub>'s proposed pathways were inspired by prior research: [64–66] 2CO<sub>2</sub> + 2e<sup>-</sup> is the answer! Seven times the amount of C<sub>2</sub>O<sub>2</sub>, that is. There are eight times as many carbon dioxide molecules as there are carbon dioxide molecules in a molecule of carbon dioxide. It's either 2CO<sub>2</sub> + 3 C (9) or 3CO<sub>2</sub> + 4e<sup>-</sup> (10) Assuming that the electrochemical pathway in Na-CO<sub>2</sub> batteries follows these chemical equations, 2CO<sub>2</sub> + 3 e<sup>-</sup> (10) It's the cathode electrode: 4Na + 3CO<sub>2</sub> e<sup>-</sup> Temperature 2Na<sub>2</sub>CO<sub>3</sub> + C (11) ANODE ELECTRODE: Na → Na<sup>+</sup> + e<sup>-</sup> (12) As a whole: 4Na + 3CO<sub>2</sub> → 2Na<sub>2</sub>CO<sub>3</sub> + C. (13) As a result, we now have a clearer picture of the chemical and electrochemical processes taking place in Na-O<sub>2</sub> and Na-CO<sub>2</sub> batteries. According to the different mechanisms, recent research progress and future perspectives will be discussed in subsequent sections regarding the rational design of the air cathode materials, Na anode protection, and electrolyte. These aspects are critical for achieving high-performance Na-O<sub>2</sub> and Na-CO<sub>2</sub> batteries, and for the practical applications of true sodium–air batteries.

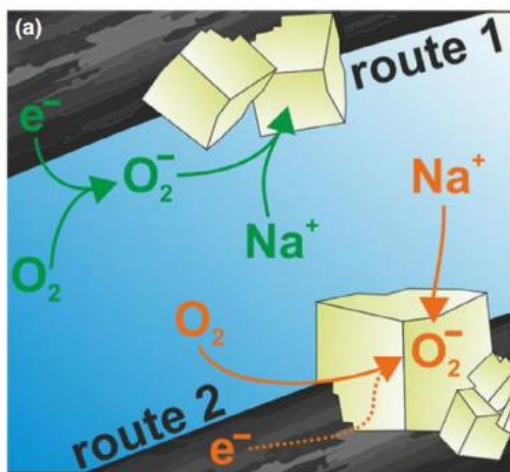
### Reaction mechanism of Na-CO<sub>2</sub>

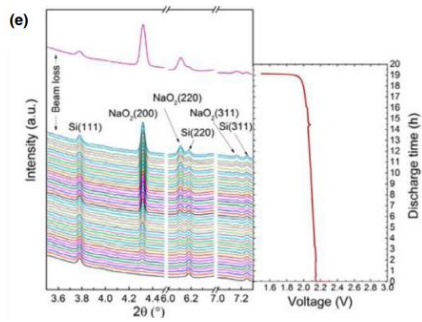
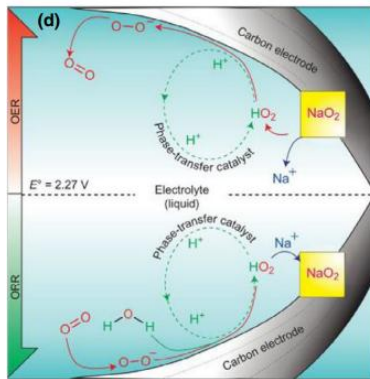
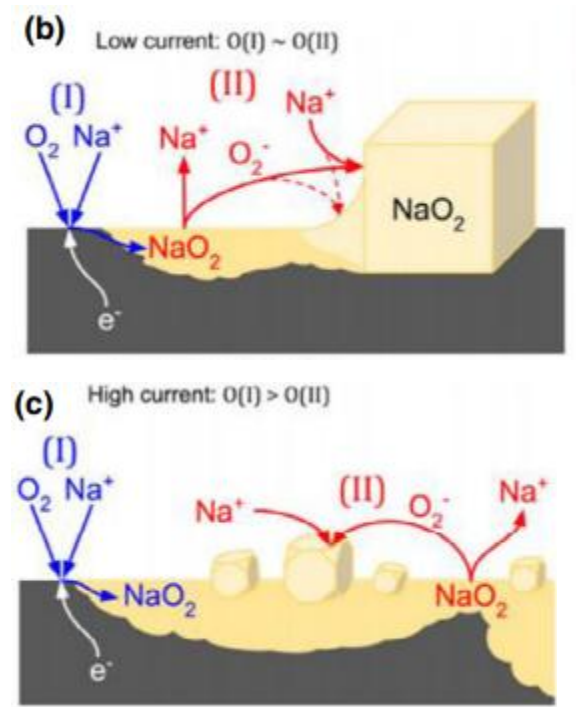
batteries With pure CO<sub>2</sub> as a reaction gas, Na<sub>2</sub>CO<sub>3</sub> is detected as a discharge product in Na-CO<sub>2</sub> batteries, as shown above. [41,62,63] Polycrystalline Na<sub>2</sub>CO<sub>3</sub> and amorphous carbon are formed when CO<sub>2</sub> molecules are reduced at the cathode and interact with sodium ions during the discharge process. There follows a charging process in which Na<sub>2</sub>CO<sub>3</sub> and amorphous carbon disintegrate reversibly and CO<sub>2</sub> is released. [41] Hu et al.[42] constructed an in situ capable Raman battery for the first study on Na CO<sub>2</sub> batteries using pure CO<sub>2</sub> as the cathode gas. While charging and discharging, Na<sub>2</sub>CO<sub>3</sub> emerged and rose in vibrational frequency at 1180 cm<sup>-1</sup>; this peak then faded away during the subsequent charging operation.

## 3. Material Design of Air Cathodes

### 3.1. Air cathodes of Na-O<sub>2</sub> batteries

Discharge products on the air cathode side of Na-O<sub>2</sub> batteries are thought to influence their specific capacity. When discharge products cover the air cathodes in Na-O<sub>2</sub> batteries, the battery's capacity is limited by the cathode's ability to conduct electricity. As with Li-O<sub>2</sub> batteries, this dependency on air cathode capability is a critical factor in Na-O<sub>2</sub> batteries' electrochemical performance. Air cathodes for Na-O<sub>2</sub> batteries may currently be made from a variety of materials, including carbon-based compounds, transition metal-based materials, noble metal-based materials, and composites of these materials. The development of an adequate supply of oxygen





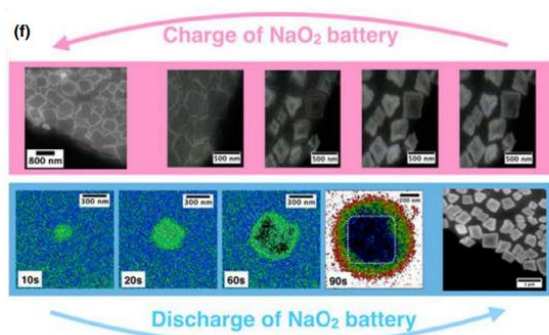


Figure 2. a) NaO<sub>2</sub> increase by solution precipitation. Excerpted with the author's permission. [57] The American Chemical Society owns the copyright to this work. Cubic NaO<sub>2</sub> crystals are discharged at b) low and c) high current rates, according to a proposed mechanism. This image has been used with permission. [58] Copyright 2017 American Chemical Society. All rights reserved. d) A diagram of the proton phase-transfer catalysis process. Permission granted to republish. [59] Springer Nature is the copyright holder. Diffraction patterns ( $\lambda = 0.207 \text{ \AA}$ ) and the corresponding galvanostatic discharge profile (recorded under in operando circumstances during the initial discharge of Na-O<sub>2</sub> cells employing 0.5 m NaCF<sub>3</sub>SO<sub>3</sub> in diglyme as electrolyte) are shown in the waterfall plot (e). [60] Copyright 2017 American Chemical Society. All rights reserved. f) Animated TEM pictures show the development of NaO<sub>2</sub> cubes during discharge and their disintegration during recharge. [61] Attribution-NonCommercial-ShareAlike Na-O<sub>2</sub> batteries with high energy density may theoretically be powered by electrodes with appropriate nanostructured topologies. Material design techniques for air cathodes and their performance in Na O<sub>2</sub> batteries will be discussed in detail below.

### Carbon-based oxygen cathodes

For chemical and electrochemical reactions to occur during the discharge and charge processes, an ideal oxygen electrode should be porous with a wide surface area for oxygen/electrolyte transport. With their large surface area, porous frameworks, and superior electronic conductivity, carbon materials have been widely used as oxygen cathodes in Na-O<sub>2</sub> batteries because of their advantages of more active surface and space for discharge product accommodation, rapid mass diffusion and efficient electron transfer. Different carbon-based materials, including as graphene [47], carbon nanotubes [67], and diamond-like crystalline carbon thin films, have been used as air cathodes for Na-O<sub>2</sub> batteries. Sun et al.[31] employed carbon thin film as an oxygen cathode for their first effort at a nonaqueous rechargeable Na-O<sub>2</sub> battery using a carbonate-based electrolyte (Figure 3a). The major discharge product, Na<sub>2</sub>O<sub>2</sub>, was identified using X-ray diffraction (XRD) examination. The discharged cathode was also discovered to include Na<sub>2</sub>CO<sub>3</sub>, NaOCO-R, and other carbonate salts, such as Na<sub>2</sub>CO<sub>3</sub>. When cycling, carbonate-based electrolytes become unstable, making them a poor choice for metal-air batteries. [68] When Hartmann et al.[32] experimented with an air cathode made of carbon fibre, they utilised 0.5 M NaCF<sub>3</sub>SO<sub>3</sub> in diethylene glycol dimethyl ether (DEGDME) as the electrolyte. Solid discharge products in their system were found to be crystalline NaO<sub>2</sub> with macroscopically cubic symmetry (Figure 3b). Low voltage overpotential discharged/charged the Na-O<sub>2</sub> cell throughout this one-electron transfer event. Additionally, graphene is used as an air electrode for Na-O<sub>2</sub> batteries, which was first used in 2013 by Liu et al. [47] Even though it was only used for 10 cycles at a current density of 300 mA g<sup>-1</sup>, the Na-O<sub>2</sub> battery was able to reach a high discharge capacity of 8268 mA h g<sup>-1</sup> at a current density of 200 mA g<sup>-1</sup>. In the context of Na-O<sub>2</sub> batteries, graphene seems to be a viable option for air electrodes. In order to boost the density of active sites for chemical adsorption and intermediate reactions, heteroatom doping of graphene sp<sup>2</sup> lattice is an efficient technique. [69] After adding nitrogen to graphene, Li et al.[48] found that the material's discharge capacity was two times more than when it was pure. They ascribed the enhanced performance of nitrogen doped graphene in Na-O<sub>2</sub> batteries to the active sites created by the nitrogen doping process. Zhang et al.[70] used a solvothermal approach to create a free-standing three-dimensional nitrogen-doped graphene aerogel material on nickel foam. Introducing nitrogen groups to the three-dimensional graphene allowed the in situ development of well-dispersed Na<sub>2</sub>O<sub>2</sub> nanoparticles, which were beneficial in reducing the charge overpotential to roughly 1 V and improving electrochemical performance. An important class of carbonaceous materials known as an air cathode for Na-O<sub>2</sub> batteries is carbon nanotubes. For Na-O<sub>2</sub> batteries, Jian et al.[67] employed a carbon

nanotube paper electrode without any binders or additives, and this resulted in a high discharge capacity of 7530 mA per gramme per hour. For Na-O<sub>2</sub> batteries, carbon nanotube paper is a promising cathode since the predominant crystalline discharge product is Na<sub>2</sub>O<sub>2</sub>·2H<sub>2</sub>O, which decomposes in the subsequent charging process. In addition, Zhao et al. constructed a large-surface-area VACNT network that is vertically oriented. [71] A large capacity might be achieved by directing the formation of nanosized NaO<sub>2</sub> particles. In a 100-cycle cycle, the cells may use as much as 90% of the electrical energy they consumed because of the kinetically advantageous electrochemical splitting of NaO<sub>2</sub>.

An air electrode made of vertically grown nitrogen-doped carbon nanotubes on carbon paper was manufactured and tested by Yadegarietal.[72] in another research effort. [72] (Figure 3c). Adding nitrogen to the carbon nanotube matrix improved its catalytic activity, and the stable nanostructure of aligned carbon nanotubes also helped with rate performance and cycle stability, as they found out. Carbon nanotubes doped with nitrogen have been used by Sun et al.[73] as an air cathode in Na-O<sub>2</sub> batteries (Figure 3d), and the researchers found that the nitrogen-doped carbon nanotubes were superior than virgin carbon nanotubes (CNTs). To achieve a greater rate capability and a longer cycle life, Na-O<sub>2</sub> batteries with the NCNTs electrode showed that nitrogen doping boosted catalytic activity, but also that the strong networks of NCNTs allow quick mass transit as well as uniform coverage of discharge products. More porous carbon materials have been produced to test their electrochemical performance in Na-O<sub>2</sub> batteries. Sun et al.[45] used a chemical vapour deposition process to create hierarchical porous carbon spheres (PCSs), as shown in Figure 4a. A high discharge capacity of 16,500 mA g<sup>-1</sup> at 500 mA g<sup>-1</sup> and good rate performance, as well as extended cycling stability up to 400 cycles with a low overall charge/discharge overpotential of around 400 mV, were obtained when it was utilised as an air cathode (Figure 4b). Nanopores within each carbon sphere, as well as macro holes produced between the two, were ideal for allowing electrolyte and oxygen to enter the inside of the spheres, allowing for the production and disintegration of film-like NaO<sub>2</sub> (Figure 4c).

### Transition metal-based oxygen cathodes

Additionally, transition metal-based air cathodes with increased electrochemical performance may be developed, as well as other carbon-based materials with significant prospects for Na-O<sub>2</sub> batteries. This has led to the development of a number of different types of transition metal-based catalysts, including transition metal compounds (NiCo<sub>2</sub>O<sub>4</sub> and CaMnO<sub>3</sub>), transition metal oxides (Co<sub>3</sub>O<sub>4</sub> and MnO<sub>2</sub>), and catalysts dispersed on nanostructured carbon (Co embedded nitrogen doped carbon fibers[52]) for Na-O<sub>2</sub> batteries, as well as other types of transition metal-based materials. A carbon and binder-free air cathode for Na-O<sub>2</sub> batteries was first developed by Liu et al.[80] by fabricating a NiCo<sub>2</sub>O<sub>4</sub> nanosheets/Ni foam composite using a simple solvothermal method, in which Ni foam served as the substrate and current collector, providing space for the deposition of discharge products. An initial discharge capacity of 1762 mA h g<sup>-1</sup> with an overpotential of 0.96 V and the discharge products Na<sub>2</sub>O<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> was attained with the composite electrode. When Hu and his colleagues annealed the CaMn(CO<sub>3</sub>)<sub>2</sub> solid solution precursor, they were able to synthesis CaMnO<sub>3</sub> with a micro and nanostructure.

A substantial discharge capacity of 9560 mA h g<sup>-1</sup> and remarkable cycling stability up to 80 cycles were achieved when the porous CaMnO<sub>3</sub> was utilised as an air cathode in Na-O<sub>2</sub> batteries. Figures 5a,b demonstrate this. Porous cobalt boride (CoB) nanosheets with high catalytic ability and improved electronic conductivity were synthesised as air cathodes by Ma et al.[76] using a simple and solid-state reaction technique. Because of its high specific capacity of 11,482 mA h g<sup>-1</sup> and extended cycle life of 74 cycles with NaO<sub>2</sub> and Na<sub>2</sub>O<sub>2</sub> as discharge products, it was used as an air cathode in the Na-O<sub>2</sub> battery, where it demonstrated outstanding electrochemical performance. Calculations using density functional theory (DFT) were used to determine why the overpotential reduced. An interaction between CoB and the Na<sub>2</sub>O<sub>2</sub>/interface shows strong O-O bonds, which may progressively promote solid–solid interface reactions until all the adsorbed discharge products were dissolved, further reducing the charging potential to 0.6V. Furthermore, air cathodes with outstanding performance need wide surface areas to accommodate discharge products, but also high conductivity to speed the breakdown of discharge products. Because of this, materials composed of transition metal catalysts and nanostructured carbon materials have been developed to manufacture effective air cathodes for Na-O<sub>2</sub> batteries. These materials. Freestanding N doped carbon fibres (Co-ECNCFs) with embedded and coated Co nanoparticles (Figure 5c) were manufactured using an electron beam spinning process by Ma et al[52]. To obtain low charge overpotential and extended cycling stability of up to 112 cycles, the Co-ECNCFs were used as a binder-free oxygen cathode for Na-O<sub>2</sub> batteries, which was better than the electrochemical

performance of NCFs without the integrated Co nanoparticles. XPS revealed some oxidation of the Co nanoparticles, but only a minor amount.

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