



Review

Superoxide-based Na-O₂ batteries: Background, current status and future prospectsXiaoting Lin^a, Qian Sun^a, Jung Tae Kim^a, Xifei Li^b, Jiujun Zhang^{c,d}, Xueliang Sun^{a,*}^a Department of Mechanical and Materials Engineering, University of Western Ontario, London, Ontario N6A 5B9, Canada^b Xi'an Key Laboratory of New Energy Materials and Devices, Institute of Advanced Electrochemical Energy & School of Material Science and Engineering, Xi'an University of Technology, Xi'an, Shanxi 710048, China^c College of Material Science and Engineering, Fuzhou University, Fujian 350108, China^d Institute for Sustainable Energy/College of Sciences, Shanghai University, Shanghai 200444, China

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ABSTRACT

Na-O₂ batteries are considered a promising energy storage device for powering next-generation electric vehicles, due to their high theoretical energy density, high energy efficiency, and low cost. Furthermore, Na-O₂ batteries that have sodium superoxide as their discharge product are highly attractive as they exhibit extremely low charge overpotentials. Though significant advances have been made on superoxide-based Na-O₂ batteries, the practical application of this technology is still severely hindered by insufficient achievable capacities and limited cycling performance. This review presents a comprehensive summary of superoxide-based Na-O₂ batteries, beginning with an overview of their configuration, historical development, and technical challenges, followed by their discharge/charge reaction mechanisms discussed in light of recent findings. Furthermore, the development of air electrodes, electrolytes, and the Na anode, as well as the detrimental effect of O₂/O₂ crossover are discussed. Finally, a general conclusion and perspective on the current limitations and recommended future research directions of Na-O₂ batteries is presented. This review aims at serving as a guideline for the development of superoxide-based Na-O₂ batteries with high energy density and long cycle life for next-generation applications such as electric vehicles.

1. Introduction

The burgeoning environmental concerns which stem from the rapid depletion of non-renewable energy sources has made it vital to reduce the earth's dependence on fossil fuels. As such, there has been a surging demand to develop green and sustainable energy technologies that are powered by renewable energy sources such as solar, tide, and wind energy. Though many systems have been developed to efficiently harness these clean energy sources, their intermittent nature significantly hinders dispatchable energy generation, making it difficult to satisfy the fluctuating demand for electricity [1,2]. Consequently, there has been on-going global efforts to develop advanced energy storage systems that can help bridge the gap between the intermittency and dispatchability of these renewable energy sources. In particular, electrochemical secondary batteries have been considered one of the most viable options for clean energy storage, due to their high energy conversion efficiencies and environmentally innocuous character. Since

their commercial introduction by Sony in 1991, Li-ion batteries (LIBs) have played a vital role in leading a wireless revolution by enabling portable electronics such as laptops and cellphones [3]. Still, this LIB technology continues to dominate the battery industry, despite their fast approaching theoretical energy density limitation. Thus, many efforts are being made to discover new battery chemistries that can outperform the current state-of-the-art and be applied to next-generation applications such as electric vehicles (EVs) [4–6].

Among the numerous emerging battery technologies, non-aqueous metal-oxygen (Li/Na-O₂) batteries have attracted tremendous interests due to their ultrahigh theoretical energy densities, which are among the highest among currently known battery chemistries [7]. Li/Na-O₂ batteries operate based on conversion reactions, using environmentally friendly and inexhaustible oxygen as the cathode material, which make these battery systems promising candidates especially for EV applications. Though the Na-O₂ battery system exhibits relatively lower theoretical energy densities in comparison to the Li-O₂ system, the low

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charging overpotential of superoxide based Na-O₂ batteries has deemed them an attractive alternative. The low charge overpotential in Na-O₂ batteries originates from the reversible oxygen/superoxide (O₂/O₂⁻) electrochemistry, different to the semi-irreversible oxygen/peroxide (O₂/O₂²⁻) redox pair in Li-O₂ batteries, resulting in a high energy utilization efficiency [8]. Furthermore, the high availability (sixth most abundant element in the earth's crust) and low cost of sodium element makes the development of Na-O₂ batteries highly practical from a resource standpoint [9].

Significant efforts have been devoted to investigating the detailed chemistry and electrochemistry of Na-O₂ batteries, including the cause of cell performance degradation. Compared to other types of Na-O₂ batteries which produce sodium peroxide or other discharge products, superoxide-based Na-O₂ batteries are more attractive due to their low charge overpotentials and effective operation without the need of a catalyst. Great progress has been made on the superoxide-based Na-O₂ battery system through the development of efficient electrodes, stable electrolytes, and novel cell configurations. However, recent studies suggest that the unique electrochemistry of superoxide-based Na-O₂ batteries also gives rise to several challenges, including the chemical instability of sodium superoxide, clogging/degradation of air electrodes, decomposition of organic electrolyte, Na anode corrosion, and oxygen/superoxide crossover. The above-mentioned issues severely impede Na-O₂ cell performance, resulting in insufficient achievable capacities and limited cycle life. Thus, a comprehensive analysis of the interplay between Na-O₂ battery components and its relation to cell performance is greatly needed.

Compared to the previous review articles which have mainly summarized strategies for non-aqueous Na-O₂ battery optimization and resulting progress [10–12], this comprehensive review focuses on superoxide-based Na-O₂ batteries. In this review, we first present the cell configuration, history, and challenges of Na-O₂ batteries. Afterwards, considerable emphasis is then placed on the current state of superoxide-based Na-O₂ cells with respect to mechanistic understanding concerning Na-O₂ chemistry and the novel design of the cell components such as the air electrode, electrolyte, and Na anode. Finally, we provide concluding perspectives by discussing aspects that have been insufficiently explored yet, however are also important for enhancing the electrochemical performance of Na-O₂ batteries. This review aims to probe a deeper understanding of the mechanism and control of NaO₂ formation and establish guidelines towards the rational design of electrodes and electrolytes for high-performance Na-O₂ cells.

2. Developmental history of superoxide-based Na-O₂ batteries

2.1. Configuration of Na-O₂ batteries

A typical Na-O₂ battery consists of a metallic Na anode, an air electrode primarily based on porous carbon, and an electrolyte layer such as a separator soaked in a Na⁺ conducting electrolyte and/or a solid-state electrolyte (SSE). The Na-O₂ battery functions based on conversion reactions, which differs from the intercalation mechanism in Na-ion batteries. The overall electrochemical reactions for O₂ at the air electrode during discharge and charge are the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER), respectively. Upon discharge, the Na metal anode is oxidized to generate Na⁺ in the electrolyte, whereas at the cathode side the O₂ is reduced to O₂⁻ and/or O₂²⁻ on the air electrode surface, combining with Na⁺ to form discharge products. On charge, the discharge products decompose with Na metal plating at the anode and O₂ evolves at the air electrode. Two-electron transfer during the ORR process of non-aqueous Li-O₂ batteries indicates the formation of Li₂O₂ as the only discharge product. In contrast, one- or two-electron transfer ORR pathways occur in Na-O₂ batteries with the formation of NaO₂ or Na₂O₂ as the discharge product. The theoretical energy densities of non-aqueous Na-O₂ batteries are approximately 1108 and 1605 Wh Kg⁻¹ considering NaO₂ and Na₂O₂ as

the discharge products, respectively.

2.2. Initial studies on Na-O₂ batteries

High temperature Na-O₂ batteries were first proposed by Peled et al. in 2010 using a liquid Na anode and polymer electrolyte at 105 °C [13]. Soon after, the first report of room-temperature Na-air batteries using a non-aqueous electrolyte was demonstrated by Fu and co-workers in 2011 [14]. The specific capacities of air electrodes are highly superior to the intercalation-based cathodes used in rechargeable Li/Na-ion batteries, demonstrating the potential of Na-air batteries as possible alternatives to Li/Na-ion batteries. In this work, crystalline Na₂O₂ and amorphous sodium carbonate were identified as the major discharge products of the constructed Na-air batteries, which used ethylene carbonate/dimethyl carbonate as an electrolyte solvent. The first superoxide-based Na-O₂ battery was demonstrated by Hartmann et al. in 2012 [15]. As a major breakthrough, they reported a low overpotential of less than 200 mV during charging, benefiting from the reversible formation and decomposition of NaO₂ via a single-electron transfer process in an ether-based electrolyte. The charge overpotential of this Na-O₂ battery is about 3–4 times lower than that ever reported for both Li-O₂ and peroxide-based Na-O₂ batteries [14,16].

In Li-O₂ batteries, LiO₂ has been identified as a transient intermediate which is unstable at room temperature and quickly converts to Li₂O₂ via electrochemical reduction or disproportionation [8]. Early on, the general battery mechanism of Na-O₂ batteries was assumed to be analogous to that of the Li-O₂ battery system. However, Hartmann et al.'s work highlighted intriguing differences between the two battery systems with the formation of NaO₂. In Na-O₂ batteries, Na⁺ ions exhibit higher polarizability compared to Li⁺ ions and thus can more effectively stabilize O₂⁻, resulting in NaO₂ precipitation as the discharge product [1]. In 2014, the reaction mechanisms of the Na-O₂ battery was predicted by Lee et al. using a first-principle calculation and by using a Li-O₂ cell as a comparison [17]. They reported that the lower charge overpotential of the Na-O₂ battery in comparison to the Li-O₂ cell was related to a lower minimum energy barrier for NaO₂ decomposition than that of Li₂O₂ decomposition. In the same year, McCloskey et al. reported that the reactivity differences between Li₂O₂ and NaO₂ may be responsible for the observed charge overpotential difference between the Li-O₂ and Na-O₂ battery systems [18].

Compared to other discharge products, NaO₂ proves to be very attractive as the reversible O₂/NaO₂ electrochemistry leads to a low charge overpotential [17,23,24]. The pioneering work conducted by Hartmann et al. laid the foundation for the superoxide-based Na-O₂ batteries, attracting extensive attention to the system [19,23,25–27]. Though the superoxide-based Na-O₂ technology has great potential to achieve batteries with high energy density and round-trip energy efficiency, the system still suffers from significant challenges and is yet far from meeting practical applications. First, steering the electrochemical reaction pathway towards desirable NaO₂ formation is a formidable challenge (Fig. 1a). In addition, the achievable specific capacity and cycling performance of current Na-O₂ batteries do not meet the strict performance requirements for commercial applications (Fig. 1b and c). The challenges of superoxide-based Na-O₂ batteries are closely related to the intrinsic properties of the cell components and external environmental influences, which are summarized in detail in Fig. 1d. The link between these issues and the substandard performance of the Na-O₂ battery needs to be clarified and addressed in order to make this next-generation technology feasible.

3. State-of-the-art research focus on superoxide-based Na-O₂ batteries

3.1. Mechanistic aspects of superoxide-based Na-O₂ electrochemistry

The mechanism of the reversible formation and decomposition of

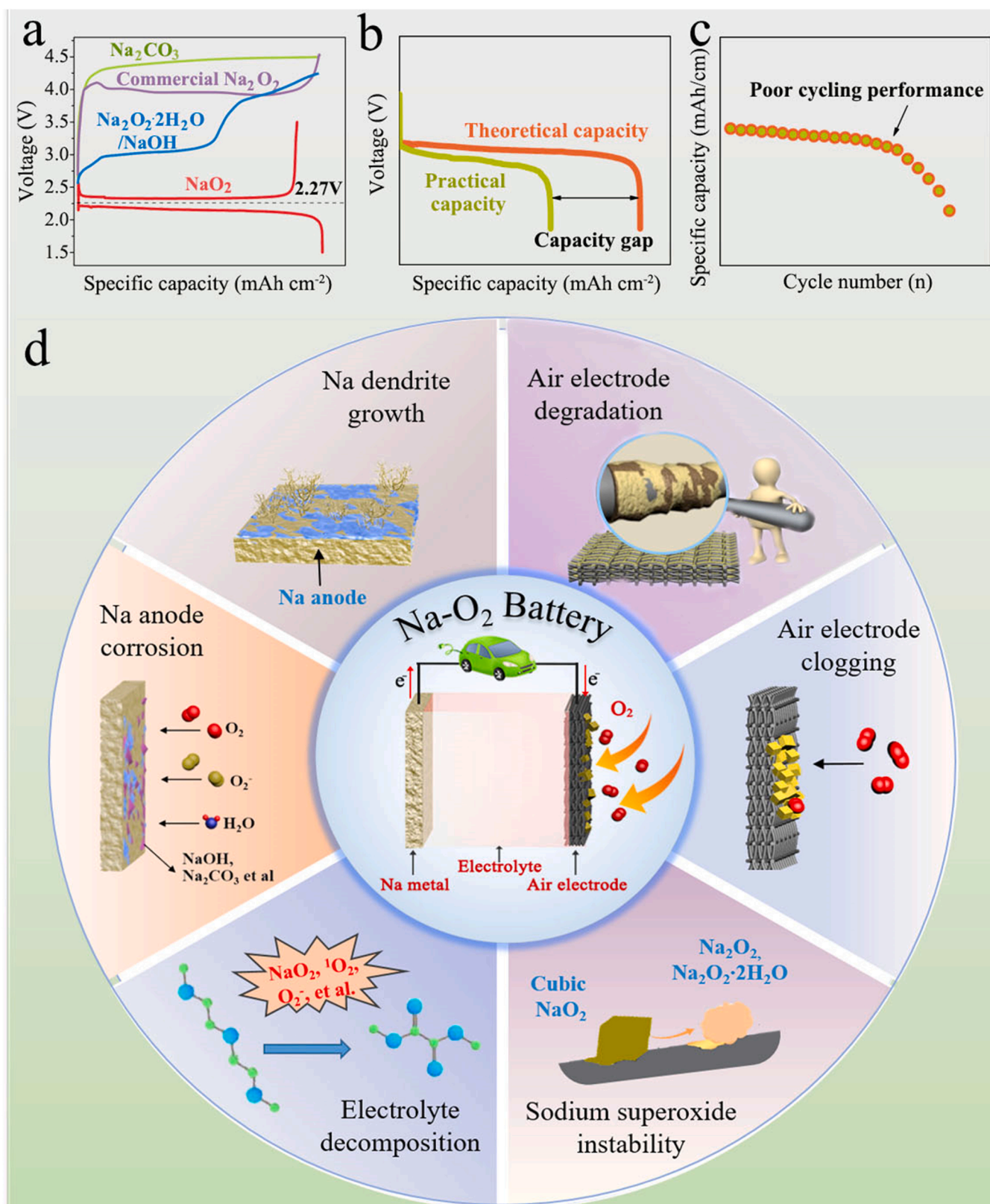


Fig. 1. Schematic diagram of the major performance deficiencies (a) controlling the NaO₂ formation [19–22], (b) low achievable capacity, (c) poor cycling performance, and (d) key issues of superoxide-based Na-O₂ battery.

NaO₂ is at the fundamental core of superoxide-based Na-O₂ batteries. Although the electrochemical reaction for NaO₂ formation seems simple, the elemental steps are complicated and the electrochemistry of Na-O₂ batteries is still elusive. Unveiling the nature of the discharge/charge process in Na-O₂ batteries is a crucial step towards the commercialization of this novel battery technology. In this section, we provide an overview of the fundamental knowledge and state-of-the-art proposed mechanisms for the ORR and OER of superoxide-based Na-O₂ batteries from a broad source of references, as well as our insights on the electrochemistry of this battery system.

3.1.1. Controlling the formation of NaO₂

In Na-O₂ batteries, elucidating the factors that govern the mechanism of O₂ reduction towards NaO₂ formation is crucial for maintaining a low charge overpotential. The formation of NaO₂ via a one-electron ORR process is kinetically preferred over two-electron transfer towards Na₂O₂ formation, while the Na₂O₂ is thermodynamically favored to form over NaO₂ [15]. Based on theoretical calculations, Kang et al. stated that NaO₂ is more stable than Na₂O₂ at the nanoscale, and the nucleation of NaO₂ is thermodynamically favored due to its lower surface energy [28]. Despite this, the understanding regarding the electrochemistry of the Na-O₂ battery system is far from being complete, and directing NaO₂ or Na₂O₂ formation in Na-O₂ batteries is still an unsolved problem. It has been experimentally proven that the oxygen electrochemistry is dependent on a wide range of factors, including the properties of electrolyte solvents, surface chemistry and electrocatalytic activity of the air electrodes, gas atmosphere, and cell configurations. In this section, we will review previous works to provide insight on cell parameters that determine NaO₂ formation during the ORR process.

The properties of the organic electrolyte are crucial for controlling NaO₂ formation in Na-O₂ batteries. Initial studies based on non-aqueous Na-O₂ batteries typically employ organic carbonate-based electrolytes, which has shown to decompose irreversibly at the cathode to form various by-products, with no evidence of NaO₂ formation [14,21]. By investigating the mechanism of oxygen reduction with various

non-aqueous electrolytes, Zhao et al. found that the ether-based electrolytes are more stable against superoxide intermediates in comparison to other electrolytes, with the predominant yield of NaO₂ upon discharge [29]. They further mention that the enhanced chemical stability of the ether solvent can be attributed to its high acid dissociation constant (pKa) (Fig. 2a). In another study, Aldous and colleagues stated that the solvents ability to form and remove $[\text{Na}^+ - \text{O}_2]_{\text{ads}}$ can influence the Na-O₂ cell chemistry, which is closely related to the donor number (DN) of the solvents [30]. For solvents with high DN, large NaO₂ particles form via a solution-precipitation path due to the strong solvation of the Na⁺ by coordination with the solvent molecular [35]. In a low DN solvent, Na⁺ is not strongly solvated and incapable of forming an ion pair interaction with O₂. Subsequently, further oxidation of O₂ occurs with the formation of Na₂O₂ on the electrode surface (Fig. 2a). It is noted that the DN of the electrolyte salts has no major impact on the Na-O₂ cell electrochemistry, which is different from the Li-O₂ battery system [36]. On the other hand, Na-O₂ cell chemistry is less impacted by trace H₂O additive in the electrolyte, while an excess amount of H₂O can strongly affect the cell electrochemistry and result in the formation of Na₂O₂·2 H₂O, NaOH et al. [25,31,37,38]. The hydration of NaO₂ is responsible for the formation of Na₂O₂·2 H₂O, and NaOH production is proposed to be attributed to the decomposition of Na₂O₂·2 H₂O or the further reaction of Na₂O₂·2 H₂O with H₂O [21,39]. Therefore, the H₂O content in the electrolyte should be carefully controlled in order to regulate the reactions in Na-O₂ cells.

The O₂ reduction mechanism is also reported as being dominated by the chemical/electrocatalytic characteristics of the air electrodes. Commercial H2315 type carbon paper (CP) is widely used as the air electrode with the formation of crystalline NaO₂ cubes as the discharge product [15,19,27,40]. The ORR proceeds through a peroxide pathway after introducing oxygen-containing functional groups on CP, forming a conformal layer of peroxide-based products at the electrode surface (Fig. 2b) [31]. Decorating the carbon cathode with solid catalysts can also catalyze oxygen reduction through the peroxide pathway. For example, film-like NaO₂ was identified as the discharge product of a

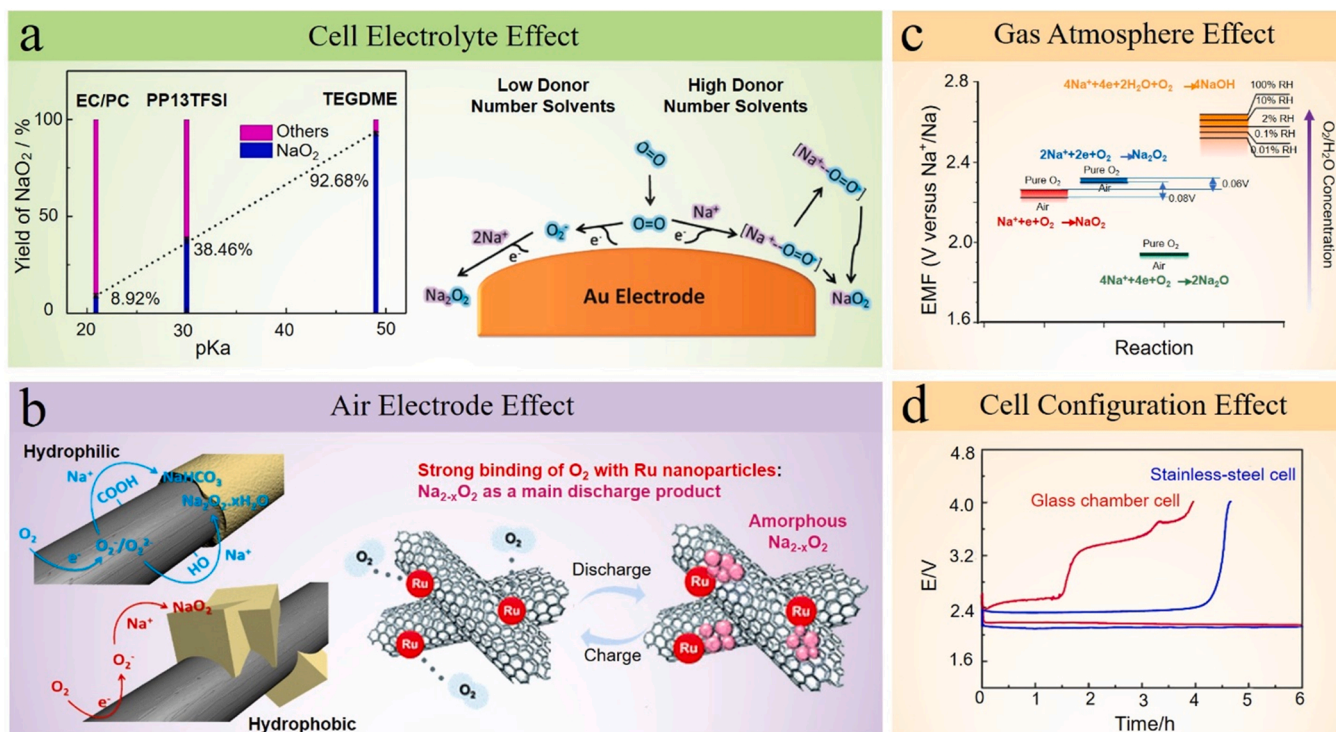


Fig. 2. The factors that affect the oxygen electrochemistry in Na-O₂ batteries including the effect of electrolyte properties (a), [29,30] effect of air electrodes functionalization and catalyst anchoring (b), [31,32] effect of the humidity in the gas atmosphere (c), [33] and effect of cell configuration (d). [34].

boron-doped reduced graphite oxide (B-rGO) cathode, while deficient sodium peroxide ($\text{Na}_{2-x}\text{O}_2$, $0 < x < 1$) with amorphous nature was obtained after introducing a micrometer-sized RuO_2 catalyst [41]. The authors attributed this phenomenon to the high affinity of the RuO_2 catalyst for O_2 . Similarly, the relatively strong interactions between the adsorbed O_2 and the Ru catalyst can also promote further reduction of O_2 and form $\text{Na}_{2-x}\text{O}_2$ on the CNT/Ru cathodes, beyond the usual reduction of O_2 to NaO_2 on the CNT cathode (Fig. 2b) [32]. More recently, Ma et al. reported that Pd nanoparticles grown on a ZnO-coated carbon cathode are capable of promoting the formation of oxygen-rich superoxide-like $\text{Na}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ through a two-electron electrochemical process [42]. In previous studies, solid catalysts have proven to be effective in accelerating the kinetics of the OER reaction and have been extensively discussed in Li- O_2 batteries and peroxide-based Na- O_2 batteries [16,43–46]. However, these catalysts cannot actively contribute to the O_2 reduction towards crystalline NaO_2 formation, which may be associated with the strong affinity of the catalysts towards O_2 , and more importantly, the high catalytic activity of the catalysts towards ORR to facilitate two-electron transfer. Based on the works reviewed above, air electrode modification via functionalization or catalyst anchoring does not always favourable for the NaO_2 formation, thus further investigation is needed.

Apart from organic electrolytes and air electrodes, the gas atmosphere and cell configurations are also critically linked to the electrochemistry of Na- O_2 batteries. H_2O is a common contaminative component in a gas atmosphere and can influence the ORR route by

inducing parasitic reactions. As reported by Zhao et al., $\text{Na}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ and NaOH can be detected when Na- O_2 batteries operate in a humid atmosphere, similar to the case of having excess amount of H_2O additive in electrolyte [39]. The effect of gas humidity on the electrochemistry and cell performance of Na-air batteries has been systematically investigated by our group (Fig. 2c) [33]. The results indicate that the Na-air battery suffers severely from H_2O content in the gas atmosphere, even more than Li-air cells, and the formation of NaOH and its derivatives are responsible for the failure of the cells. Additionally, the possible CO_2 impurities in the O_2 gas or the parasitic reactions which occur can react readily with the NaO_2 , forming Na_2CO_3 on the air electrode [33]. The O_2 intermediate is a strong nucleophile and a good charge transfer agent which can react with the CO_2 to form various peroxy carbonate species including CO_4 , CO_4^{2-} , and $\text{C}_2\text{O}_6^{2-}$ [47]. Based on the report of Qiao et al., the dominant Li- O_2/CO_2 electrochemistry switches from O_2/O_2^- to $\text{O}_2\text{-CO}_2/\text{C}_2\text{O}_6^{2-}$ when increasing the molar ratio of CO_2/O_2 in the cells atmosphere. [48] It should be noted that the H_2O and CO_2 contaminants can also be introduced into Na- O_2 batteries from leaks in imperfect cells, and even trace amounts of air leakage may result in a completely different Na- O_2 electrochemistry (Fig. 2d) [34]. Generally, Na- O_2 cells that use a dry ether electrolyte and ultrapure O_2 gas are more likely to achieve NaO_2 as the sole discharge product [19,27].

3.1.2. Formation/growth mechanism of NaO_2 during discharge

In superoxide-based Na- O_2 batteries, O_2 is reduced to form a superoxide intermediate (O_2^-) which combines with Na^+ to form NaO_2 , which

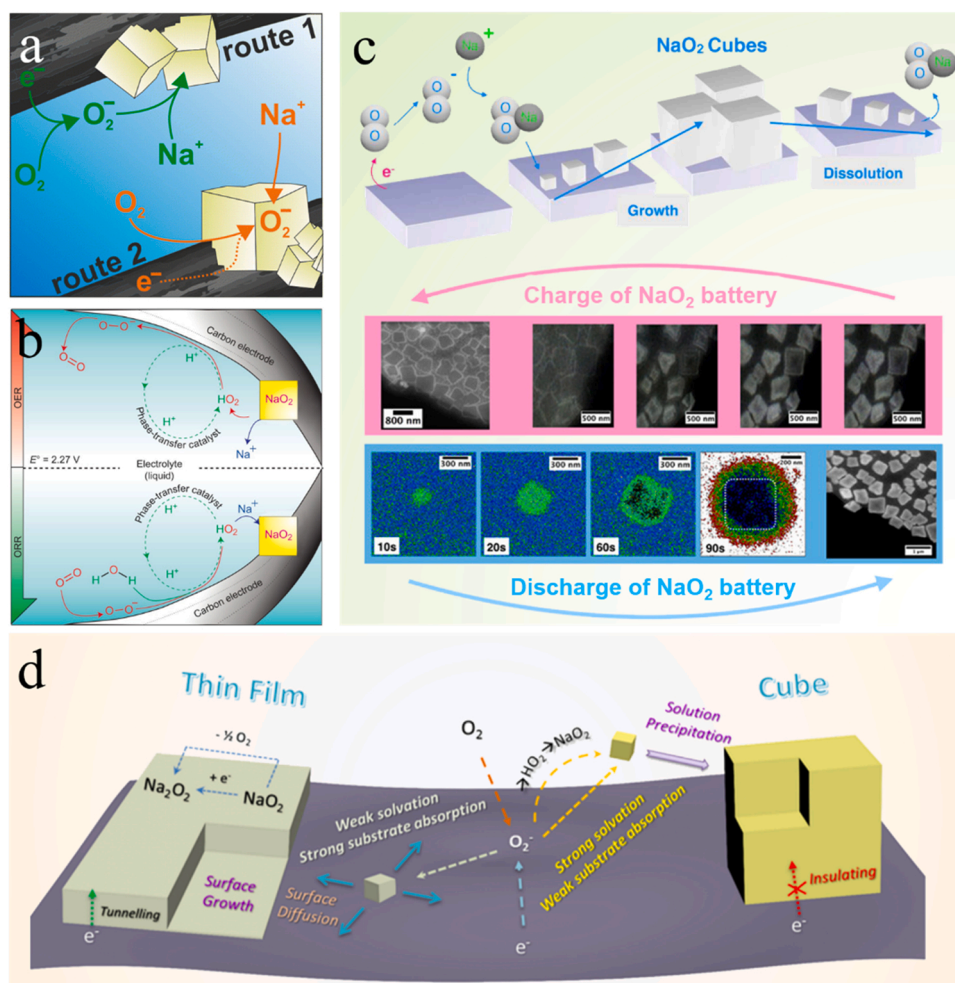


Fig. 3. The formation/growth mechanisms of large NaO_2 cubes in Na- O_2 batteries. (a) Two potential routes for NaO_2 cube growth [49]; (b) Schematic illustration of the mechanism of PPTCs during NaO_2 cubes formation [25]; (c) Schematic of the electrochemically induced discharge and charge processes obtained based on operando TEM observation [50]; (d) Schematic diagrams of catalytic $\text{CNT}@Co_3O_4$ mediated growth mechanism of NaO_2 in Na- O_2 batteries [51].

usually deposits on the air electrode as crystalline cubes in the diameter of 1–50 μm . Two mechanisms have been proposed for how these steps proceed. Solution-mediated pathway suggests that the NaO_2 cubes are formed via formation and dissolution of the O_2 intermediate from cathode surface followed by a precipitation step upon local supersaturation (Fig. 3a, route one), while the surface-mediated mechanism involves the direct reduction of O_2 to O_2^- at the NaO_2 surface and continuous growth on existing NaO_2 nucleus (Fig. 3a, route two) [49]. Great efforts have been devoted in investigating the exact pathway, and clear evidence has been obtained that supports the solution-precipitation route of large NaO_2 cube formation.

NaO_2 is predicted to be an electrical insulator based on density functional theory calculations and other techniques [49,52,53]. The insulating nature of NaO_2 makes direct electrochemical reduction of O_2 on existing an NaO_2 surface difficult to realize [53]. On the other hand, NaO_2 exhibits distinctly low nucleation and dissolution energies, enabling NaO_2 crystal growth through solution process theoretically [54]. The significant solubility of NaO_2 in a diglyme-based electrolyte (10^{-4} mol/L) further raises the possibility that the large NaO_2 cubes can grow via precipitation [49]. In 2015, Xia et al. experimentally demonstrated that the solution-mediated NaO_2 formation pathway is operative and driven by the presence of a proton phase transfer catalyst (PPTC) in the electrolyte, such as H_2O and benzoic acid [55]. As shown in Fig. 3b, the O_2 formed on the cathode could readily abstract protons from H_2O to produce highly soluble HO_2 radicals, which can migrate to the incipient NaO_2 nuclei and form NaO_2 via metathesis on encountering solvated Na^+ in electrolyte [25]. Direct evidence of solution-mediated O_2 transport from the cathode to the electrolyte was confirmed by conducting quantitative measurements on HO_2 using coupled electron spin resonance (ESR) spectroscopy in their subsequent research [27]. More recently, solution-mediated growth of NaO_2 cubes in a liquid Na-O_2 micro battery was directly visualized by using operando electrochemical transmission electron microscopy (TEM) coupled with fast imaging, as representatively shown by the time-resolved TEM images in Fig. 3c [50]. Since the ORR process requires access to both Na^+ and electrons, the observation of large NaO_2 cubes on an insulating glass fiber (GF) separator or SSE membrane gives further evidence for the solution-precipitation pathway [19,56].

Apart from large NaO_2 cubes, there have also been a few reports of NaO_2 with other morphologies/nature, such as submicrometric crystallites, films, and micrometer flakes [57–59]. The nature of NaO_2 that forms on the air electrode is intimately connected with the properties of the electrolyte, which may affect the discharge reaction mechanism via a surface or solution-mediated pathway. For example, short chain ether with weak solvent-solute interactions, which requires a low de-solvation barrier for NaO_2 formation, can facilitate the formation of large NaO_2 crystals. Long chain ethers can shift the formation of NaO_2 which follows a surface-mediated pathway, accompanying the growth of submicrometric crystallites [60]. This result differs drastically from the Li-O_2 battery system, in which the solvents' DN is the major factor in facilitating surface or solution growth of Li_2O_2 [61]. Along with solvents, trace amount of electrolyte additives have also shown to influence the NaO_2 formation/growth mechanism (Fig. 3b). The addition of PPTCs can enhance the transport of O_2 in the electrolyte and initiate the precipitation of large crystalline NaO_2 . However, in the absence of PPTC, the discharge product is confined to the electrode surface with the formation of quasi-amorphous NaO_2 thin films [25]. There have also been reports of employing a redox mediator (RM) to alter the ORR pathway in Na-O_2 batteries [62]. With the addition of a RM, the ORR takes place via the chemical reaction of O_2 with the reduced form of RM in the electrolyte. This reaction mechanism enables the transformation of O_2 reduction from the finite region near the air electrode surface to the solution-phase, facilitating the solution-based reduction of O_2 to NaO_2 during discharging.

The surface chemistry of the air electrode is another factor that has a tremendous effect on the NaO_2 growth mechanism. As reported by Lutz

et al., the introduction of Au on the carbon cathode surface results in the formation of NaO_2 thin flakes via a surface-driven growth mechanism, attributed to the increased nucleation rate due to the high surface energy and strong interaction between Au and O_2/O_2^- [58]. This conclusion also applies to the chemical precipitation of KO_2 from solution, as different KO_2 growth patterns have been observed on untreated and Au-coated carbon cathodes. In our previous work, instead of forming large NaO_2 cubes via solution precipitation, we found that the strong adsorption of atomic layer deposited Co_3O_4 catalyst towards the O_2 intermediate resulted in better surface diffusion of O_2^- and subsequent growth of the NaO_2 thin film on the $\text{CNT@Co}_3\text{O}_4$ cathode [51]. The growth mechanisms of NaO_2 on different air electrodes is illustrated in Fig. 3d. More recently, Zheng and co-workers found that pyrrolic and pyridinic-N doping in carbon nanofiber cathodes can also optimize the surface adsorption energy of the reactants and intermediate, facilitating the film-like NaO_2 layer growth on the cathode surface by tuning the NaO_2 formation route [63].

3.1.3. Decomposition mechanism of NaO_2 during charge

The charging process of Na-O_2 batteries involves the electrochemical decomposition of NaO_2 . A closer look at the charge profile shows a potential spike at the beginning followed by a steady plateau and a steep increase in voltage at the end of the recharge process. In earlier studies, Hartmann et al. introduced a kinetic model for the dissolution of a NaO_2 cube during the charging process, and the characteristic features of the charge profile can be well explained by a solution mediated oxygen evolution process [49]. Nazar's group demonstrated that the OER pathway involves the dissolution of NaO_2 and the subsequent oxidation of HO_2 ($\text{HO}_2 \rightarrow \text{O}_2 + \text{H}^+ + \text{e}^-$) at the air electrode surface in the presence of a proton donor by detecting the changes of the superoxide content upon charge using a ESR technique (Fig. 3b) [27]. The charge overpotential increased significantly when charging the NaO_2 cell in the absence of H_2O , suggesting the involvement of H_2O during the activation process of NaO_2 decomposition with a low charge overpotential. The solution-based process for the decomposition of the NaO_2 cube has also been reported by other groups [26,49,54]. However, Morasch and co-workers dismiss any solution-mediated oxidation processes since no considerable amount of soluble species can be detected when using a rotating ring disk electrode measurement in their study [64]. They further stated that the NaO_2 is conductive enough to enable direct electrochemical oxidation at the electrode/ NaO_2 cube interface, which is inconsistent with the previous results which report that bulk NaO_2 presents negligible conductivity at room temperature [49,52,53].

In fact, most researchers have pictured the solution mediated NaO_2 cubes oxidation during charging of Na-O_2 batteries. This view is broadly consistent with the high-angle annular dark-field scanning TEM (HAADF-STEM) observations of Lutz et al., who revealed the progressive decomposition of NaO_2 during charging [50]. Fig. 4a shows that the dissolution of NaO_2 cubes dissolution initializes at the NaO_2 /electrolyte interface and proceeding downwards to the air electrode surface with increasing depths of charge, accompanying the decrease of cube size. Moreover, the constant contact between the non-conducting NaO_2 cubes and the carbon electrode further suggests that OER at the NaO_2 /carbon interface is unlikely. While at the end of charging, the cubes cannot be completely decomposed with a parasitic shell of Na_2CO_3 remaining on the electrode surface. The oxidation of NaO_2 preferentially occurs on the outer surface of NaO_2 instead of the NaO_2 /carbon cathode interface, which is further supported by the transmission X-ray microscopy study that was conducted by Landa-Medrande and coworkers [66]. Similarly, a passivation layer composed of oxygen-containing side products is formed after recharging.

More recently, a detailed electrochemical charging mechanism has been revealed by our group by tracking the morphological/chemical evolution of the large micrometer sized NaO_2 cubes [65]. We found that the observed morphologies are associated with the presence of different chemical components, which decompose electrochemically at different

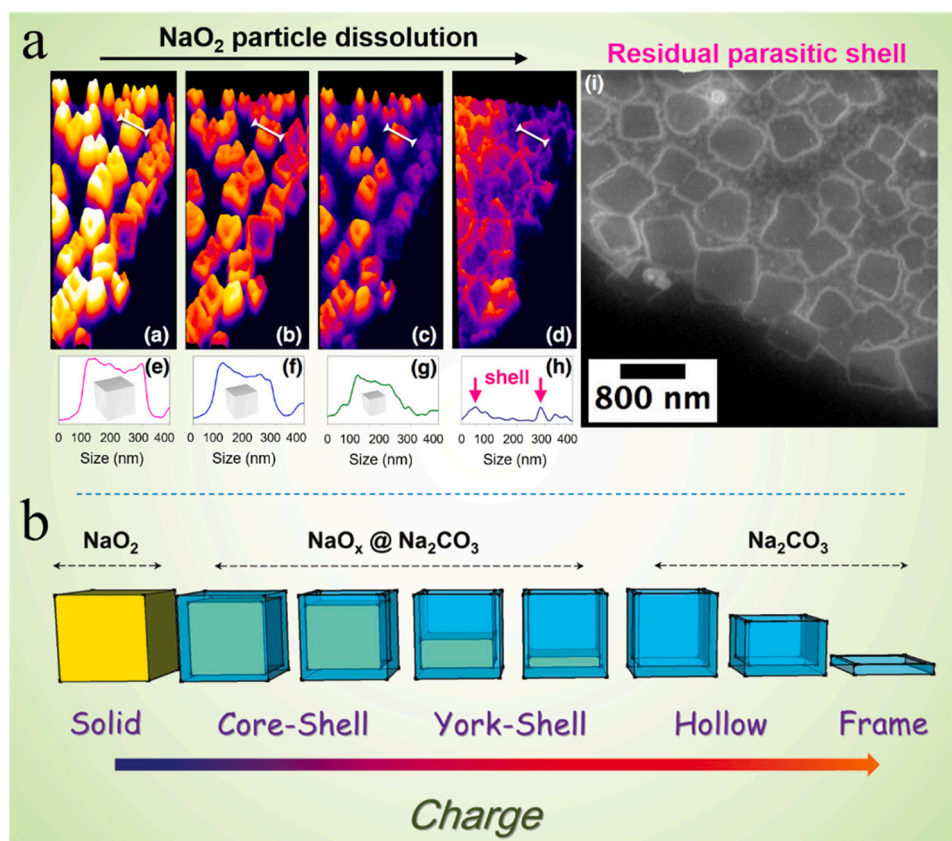


Fig. 4. The decomposition mechanism of NaO₂ cubes during charging process. (a) HAADF-STEM images at different depth of charge that depict the dissolution of the NaO₂ cubes via solution [50]; (b) The morphological and chemically compositional evolution of NaO₂ cube during recharging [65].

voltages during the cell operation (Fig. 4b). A solid cube is converted to a core-shell structure shortly after charging, and the outer layer of the cubic shape intermediate is identified as carbonate. The following charging process leads to the removal of the sodium peroxide-like phase core at a lower potential compared to the required voltage for the final removal of the Na₂CO₃ shell, resulting in yolk-shell, hollow, and frame structured interphases. These results help explain why the oxidation curve of Na-O₂ batteries is comprised of multiple voltage steps in some studies, and the high charge plateaus (≥ 3 V) are mostly caused by the parasitic shell on NaO₂ cubes [67,68]. Moreover, the parasitic shell on the outmost surface traps the NaO₂, which is partially responsible for the presence of the voltage peak at the beginning of charging and incomplete decomposition of NaO₂ after charging with a limited voltage (~ 3 V) [56,57,69].

3.1.4. Chemical stability of NaO₂ and its relevance to the charge behaviors

The reversible formation and decomposition of NaO₂ promises a high energy efficiency of Na-O₂ batteries. However, the chemical aggressiveness of NaO₂ results in its instability upon cycling or during rest in the cell environment. It is well accepted that the parasitic shell that is observed during the cell charging process is mainly caused by the reactions between NaO₂ and the liquid electrolyte/air electrode [67–70]. The parasitic shell initially appears as a thin film on the cubic structure and then gradually develop into a thick spherical shell, resulting in reversible capacity loss and decreased charging kinetics [50].

The time-dependent phase transformation of NaO₂ via chemical reactions in the cell environment has been widely reported, accompanied by electrolyte/electrode degradation to form various side products. Time-resolved X-ray diffraction (XRD) characterization indicates the gradual transformation of initial NaO₂ discharge product into Na₂O₂·2 H₂O (Fig. 5a) [31]. Besides Na₂O₂·2 H₂O, the formation of Na₂CO₃ has been identified by Rojo and colleagues using Raman and

Fourier-transform infrared spectroscopy (FTIR) characterizations, after 30 h rest in the cell environment [68]. Solid-state nuclear magnetic resonance (NMR) measurements conducted by Liu and coworkers confirmed the chemical instability of NaO₂ upon cycling using a dimethoxyethane (DME)-based electrolyte, and a mixture of sodium hydroxide, formate, carbonate, and acetate has been identified [71]. The reactivity of NaO₂ with the air electrode (polymer binder) has also been confirmed by the formation of NaF and Na₂CO₃ in the NaO₂ cell [72]. Recently, our group clarified the mechanism behind the decomposition of NaO₂ in the presence of diglyme-based electrolytes by using an in-situ Raman technique. The chemical maps of the NaO₂ cube indicate a fast degradation rate, with no superoxide being detected after 150 h (Fig. 5b). By monitoring the chemical changes of the NaO₂, we proposed that exposing NaO₂ to the cell electrolyte can induce NaO₂ degradation to form oxalate-based side products. Furthermore, we found that Na₂O₂·2 H₂O is not the thermodynamically favorable side product for NaO₂ degradation, which contrasts to some of the previous reports [26, 31,71]. This discrepancy may be related to the characterization techniques, and Na₂O₂·2 H₂O may only be formed under the high-energy beam used by the measuring probe [26,31]. On the other hand, NaO₂ can degrade and then convert to Na₂O₂·2 H₂O upon exposure to an ambient atmosphere or organic electrolyte with a large amount of H₂O [38,73]. Therefore, the airtightness of the sample holder during characterization may also explain the discrepancy of the results in different works.

The stability of NaO₂ can also be affected by other factors (Fig. 5c). For example, Liu and coworkers found that the decomposition rate of NaO₂ can be decreased after removing the Na metal anode from the cell [75]. This phenomenon is ascribed to the fact that the Na metal anode contributes to the migration of O₂ towards the anode, promoting more NaO₂ to dissolve into the electrolyte and liberate free O₂. Similarly, the consumption of O₂ via parasitic reactions on the cathode side can also

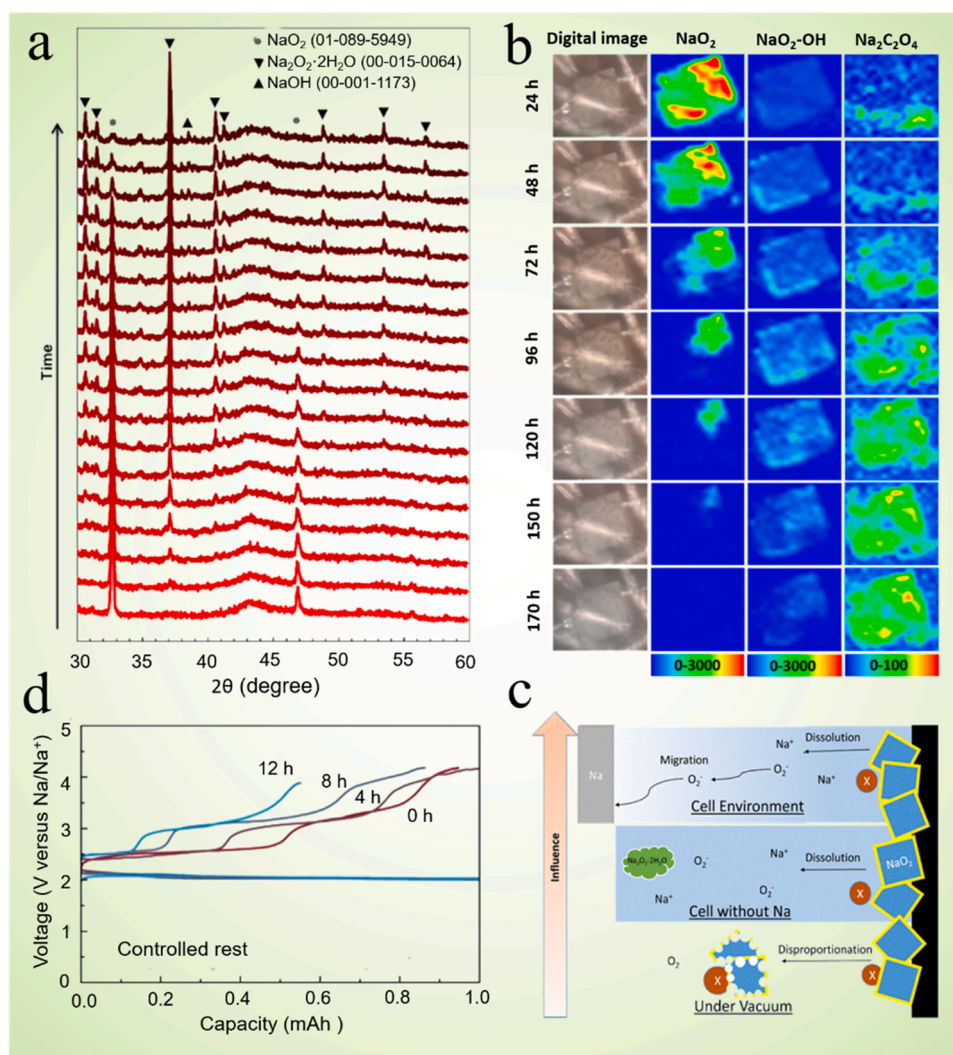


Fig. 5. The chemical instability of NaO_2 . (a) Consecutive in-line XRD patterns for air electrode discharged in a Na-O_2 cell; (b) Chemical maps reproduced from Raman spectra recorded for a NaO_2 cube on air electrode containing additional electrolyte at different time intervals [74]; (c) Schematic illustration of the instability of NaO_2 under various conditions [75]; (d) electrochemical discharge/charge profiles of Na-O_2 cells with different rest times before recharge [26].

decrease the O_2 concentration and promote the subsequent dissolution/ionization of NaO_2 in the electrolyte, contributing to the instability of NaO_2 [26]. The stability of NaO_2 is also highly related to its nature and poor crystallinity of the NaO_2 film with high electrolyte/electrode contact area has negative effects on NaO_2 stability [76]. More recently, Qian and coworkers claimed that selecting a solvent with minimum NaO_2 solubility can reduce the degradation of dissolved NaO_2 [77]. Compared with resting in the cell environment, storing NaO_2 in an evacuated pouch can significantly decrease the decomposition rate. While as an extreme reactive species, NaO_2 still undergoes disproportionating reaction even under vacuum to form $\text{Na}_{2-x}\text{O}_2$ ($0 < x < 1$) [75].

Stabilizing NaO_2 is crucial for developing high-performance Na-O_2 batteries. Undoubtedly, the consumption and transformation of NaO_2 is the origin of cause for the fast decay of cell performance and multiple charge steps. As reported by Kim et al., the NaO_2 oxidation plateau decreases with increasing rest time, accompanied by a significant decrease in the Coulombic efficiency (Fig. 5d) [26]. On the other hand, the formation of a parasitic shell results in a higher charge voltage to completely remove the remaining NaO_2 and side products [78]. While the higher charge voltage in turn aggravates the decomposition of the cells components, posing a significant challenge for achieving highly reversible and energy efficient Na-O_2 batteries [38]. Considering the many factors that influence NaO_2 degradation, the optimization of cell

components is a good strategy to stabilize NaO_2 , achieve efficient charge chemistry, and increase cell performance. Moreover, introducing functional separators to mitigate the effect of the Na anode towards O_2 migration may also contribute to enhancing the NaO_2 stability by inhibiting its dissolution.

3.2. Parasitic chemistry during battery operation

Undesirable parasitic reactions which occur at the cathode are considered one of the main obstacles for achieving high-performance Na-O_2 batteries. Thus, research that elucidates the mechanism behind these parasitic reactions is greatly needed. In Na-O_2 batteries, the parasitic reactions have traditionally been ascribed to the reactivity of reduced oxygen species that form during cell operation. Recent studies provide evidence that much of the parasitic chemistry arises from singlet oxygen ($^1\text{O}_2$), which forms at the air electrodes of Na-O_2 batteries [79]. In this section, we summarize the current findings on the highly reactive reduced oxygen species and singlet oxygen which forms in Na-O_2 batteries, which conclusively explains the mechanisms of parasitic chemistry and guide pathways to counteract the problem.

3.2.1. Reactivity of reduced oxygen species

The primary reduced oxygen species in Na-O_2 batteries are O_2^- , HOO^- ,

HOO^\cdot , and HO^\cdot , which are considered as the reactant or source of parasitic chemistry. The reactivity of the reduced oxygen species towards organic substrates stem from their nucleophilicity, basicity, and radical nature, resulting in nucleophilic substitution, as well as H^+ and H atom abstraction [80,81]. Nucleophilic attack has been considered as the primary source of parasitic reactions in Li/Na- O_2 batteries. The powerful nucleophilicity of O_2^\cdot makes it attacks the positively charged components of any organic electrolytes in the absence of a proton. As reported by Guo's group, carbonate-based electrolytes suffer from severe decomposition issues due to the nucleophilic attack of O_2^\cdot on the O-alkyl carbon, resulting in the formation of Na_2CO_3 and sodium carboxylates [29]. Ether-based electrolytes are relatively stable towards nucleophilic substitution by O_2^\cdot due to the lack of electron-withdrawing functional groups. However, O_2^\cdot can act as a strong base, proton abstraction from the solvent by the O_2^\cdot species forms HO_2 . The formation of HO_2 can induce nucleophilic attacks of the H^+ -lost solvent, resulting in the oxidative decomposition of solvent to produce by-products (CO_2 , H_2O and OH^- et al.). This is a known cause of glyme-based electrolyte

decomposition in Na- O_2 batteries (Fig. 6a) [26]. On the other hand, the reactivity of ethers toward auto-oxidation also gives rise to significant problems. The oxidation of the ether electrolyte by O_2 produces hydroperoxide, which is unstable against O_2 and rapidly decomposes into esters, carboxylates, and CO_2 . This O_2 -assisted nucleophilic attack reaction with O_2 radicals have also been reported to be a general mechanism that degrades the ether electrolyte in Li- and Na- O_2 batteries [29, 82,83].

Protic additives in the electrolytes have been introduced to enhance the Na- O_2 cell discharge capacity, while the addition of excess proton sources increases parasitic electrochemistry as well. In the presence of protic additives, HOO^\cdot , HOO^\cdot and HO^\cdot may form via following equations [61]:

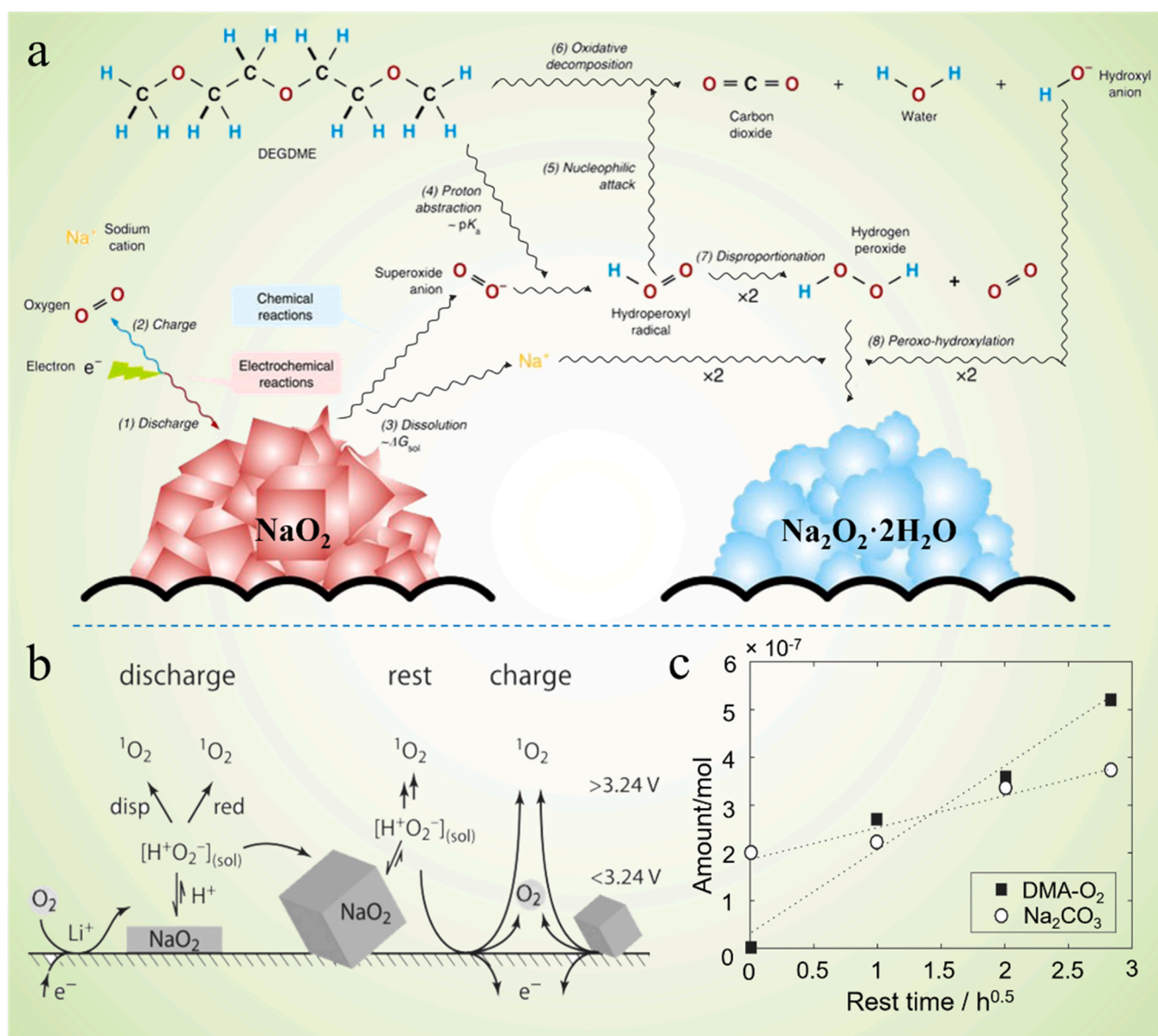


Fig. 6. The parasitic chemistry involving reduced oxygen species and singlet oxygen in Na- O_2 batteries. (a) Schematic of the mechanism illustrating the electrochemical and chemical reactions in the Na- O_2 cell [26]; (b) Schematic showing the pathways to $^1\text{O}_2$ during discharge, rest and charge, and (c) $^1\text{O}_2$ generation and parasitic chemistry during prolonged contact of the NaO_2 with the electrolyte [79].

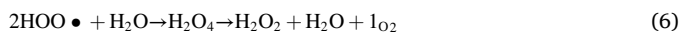


These species are more reactive than the O_2^- and can serve as promoters to increase parasitic chemistry in batteries [84]. Compared with O_2^- , the HOO^- species is a stronger base and thus can abstract a proton from a proton source more easily. Moreover, HO^\bullet can readily abstract H atoms and forms C-centered radicals, initiating thermodynamically favourable chain reactions in the presence of O_2 [82,85]. Undoubtedly, the reactivity of these species with the organic electrolyte is detrimental to the Na- O_2 cell performance.

The parasitic reactions in Na- O_2 batteries have been predominantly ascribed to the reactivity of the reduced oxygen species towards electrolyte solvents. Nevertheless, this reactivity still fails to explain the parasitic chemistry which occurs in Na- O_2 batteries. For example, the parasitic reactions during charging are much serious than that of the discharge process, which directly oppose the reactivity of O_2 . The significant increase of Na- O_2 cell lifetime after decreasing the charge cut-off voltage further forcefully demonstrates that the reactivity of reduced oxygen species with cell components is not the prime source of parasitic reactions [38]. Therefore, degradation pathways other than the reduced oxygen species attack must prevail during Na- O_2 cell operation.

3.2.2. Formation of singlet oxygen

It has been widely reported that singlet oxygen ($^1\text{O}_2$), a well-known reactive intermediate in chemistry, can be produced during Li- O_2 electrochemistry. Moreover, the electrochemical oxidation of Li_2O_2 is considered as a source of highly reactive $^1\text{O}_2$ [86,87]. Recently, the generation of $^1\text{O}_2$ has also been verified in Na- O_2 batteries, and its prevalence during cell operation has shown to have a major influence on parasitic chemistry [88]. By using chemical probes that can selectively form a stable adduct with $^1\text{O}_2$, Freunberger et al. found that $^1\text{O}_2$ was generated at all stages of Na- O_2 cell operation, exhibiting a growing rate with the rise in charge voltage [79]. Thermodynamic results indicate that the direct electrochemical NaO_2 decomposition is responsible for the $^1\text{O}_2$ generation at high charge voltages (> 3.24 V), while the singlet oxygen formation mechanism during discharge, rest, and charge below 3.24 V involves proton mediated superoxide disproportionation (Fig. 6b). This phenomenon is related to the presence of H_2O or other proton sources in the electrolytes, which leads to soluble HOO^\bullet and thus facilitates large NaO_2 precipitation via the metathesis reaction ($\text{HOO}^\bullet + \text{Na}^+ \rightarrow \text{NaO}_2 + \text{H}^+$). On the other hand, both the reduction of HOO^\bullet by the O_2^- anion and the disproportionation of HOO^\bullet can produce $^1\text{O}_2$ via the Eqs. (5) and (6), respectively [79].



Further quantitative analysis suggests that the extent of side reactions follows the occurrence of $^1\text{O}_2$, and $^1\text{O}_2$ is recognized to be responsible for a major fraction of the side products in Na- O_2 batteries using ether-based electrolytes (Fig. 6c). Similarly, the high reactivity of $^1\text{O}_2$ was proposed to be responsible for the detrimental reactions in Li- O_2 [88]. The degradation of ether-based electrolytes in Li- O_2 batteries involves the oxidation of the solvent to a mixture of Li_2CO_3 , Li acetate and Li formate, and $^1\text{O}_2$ molecule is reported to play a key role in initiating the electrolyte degradation path [83,89]. It is also revealed that the $^1\text{O}_2$ can degrade the carbon cathodes and deactivate the redox mediators that used to decrease the charge overpotential of Li- O_2 cells [90,91]. Since parasitic $^1\text{O}_2$ reactions are one of the main issues hindering the reversibility of Li/Na- O_2 batteries, preventing $^1\text{O}_2$ formation or eliminating $^1\text{O}_2$ before provoking side reactions is of significance. On one hand, introducing $^1\text{O}_2$ trapping molecular or convert $^1\text{O}_2$ to stable $^3\text{O}_2$ through physical quenching can be practically utilized to suppress side reaction in Li/Na- O_2 batteries [92]. On the other hand, tuning the

properties of cathode materials is important in alleviating $^1\text{O}_2$ production. Further, H_2O or other proton sources in organic electrolyte are identified as the main driver for $^1\text{O}_2$ formation during cell operation, which further accelerates the electrolyte degradation. Thus, water/aprotic additives in the Na- O_2 battery electrolyte are a double-edged sword, thus careful content optimization and control is needed.

3.3. Air electrodes

Along with the ambiguity regarding the electrochemistry of Na- O_2 batteries, air electrode materials also represent another major technical challenge for their development. In terms of scientific research, the ultimate goal is to achieve Na- O_2 cells with high specific capacity and long cycle life, which strongly depends on the materials and microstructures of the air electrodes. The surface chemistry of the air electrode is fundamentally important for NaO_2 formation, as discussed in Section 3.1.1. Controlling the formation of favorable large NaO_2 cubes, preventing cathode pore clogging, and minimizing air electrode degradation through rational design of the air electrode is crucial in maximizing the achievable capacity of Na- O_2 batteries.

3.3.1. Clogging/passivation of air electrodes by NaO_2

Superoxide-based Na- O_2 batteries exhibit a “sudden death” phenomenon before the pores of the air electrode are fully filled with NaO_2 , resulting in a cell capacity that falls short of the theoretical value [93, 94]. This “sudden death” is a precipitous decrease in voltage that signifies the termination of the discharge process. The mechanism of this phenomenon was found to be related to the surface passivation or pore clogging of the air electrode, which is intimately determined by the NaO_2 formation mechanisms and operating parameters.

The NaO_2 growth mechanism follows either a solution pathway or a surface pathway, and the specific mechanism has a major impact on the achievable capacity of the Na- O_2 cell (Fig. 7a). Normally, the surface-mediated pathway results in thin film-like NaO_2 formation on the air electrode. This surface passivation of the electrode surface passivation which results from NaO_2 film coverage is the major restricting factor to the cell capacity of Na- O_2 cells. In this case, a small discharge capacity can be achieved due to low NaO_2 production [58,60]. The solution-mediated mechanism facilitates the formation of micrometer-sized NaO_2 cubes, which usually leads to a relatively high discharge capacity, due to high NaO_2 production. However, because of the low diffusivity and solubility of O_2 in the electrolyte, large NaO_2 cubes preferentially deposit on the O_2 side of the air electrode. Such a distribution of NaO_2 potentially blocks the access of O_2 to the whole air electrode, resulting in underutilization of the air electrodes [19].

Reports have shown that the discharge current density is also a critical restriction factor to the “sudden death” mechanism, which is closely related to the spatial distribution of NaO_2 cubes within the air electrodes. As reported by Janek et al., the size of NaO_2 cubes decreases almost linearly with increasing current density [40]. By applying a synchrotron X-ray tomography technique, they further revealed that NaO_2 preferentially deposits on the air electrode facing the O_2 reservoir with increasing current density (Fig. 7b). These observations are consistent with the nucleation theory and the report of D. McCloskey et al. [94]. High rates lead to quick supersaturation of O_2 and high nucleation rates, resulting in diminutive NaO_2 crystals forming on the air electrode surface in a film-like manner. Under this circumstance, the “sudden death” phenomenon on discharge is caused primarily by electrode surface passivation. Conversely, at low discharge rates, large but sparsely distributed NaO_2 cubes make the cells more susceptible to failure as a result of clogged pores [35]. At a given discharge rate, the sudden death mechanism of Na- O_2 cells is highly influenced by O_2 pressure (Fig. 7c) [93]. Na- O_2 batteries that operate at low O_2 pressures are prone to failure due to electrode surface passivation. At high O_2 pressures, the batteries fail at a higher rate due to pore clogging. The transition of the cell failure mechanism is attributed to the combination

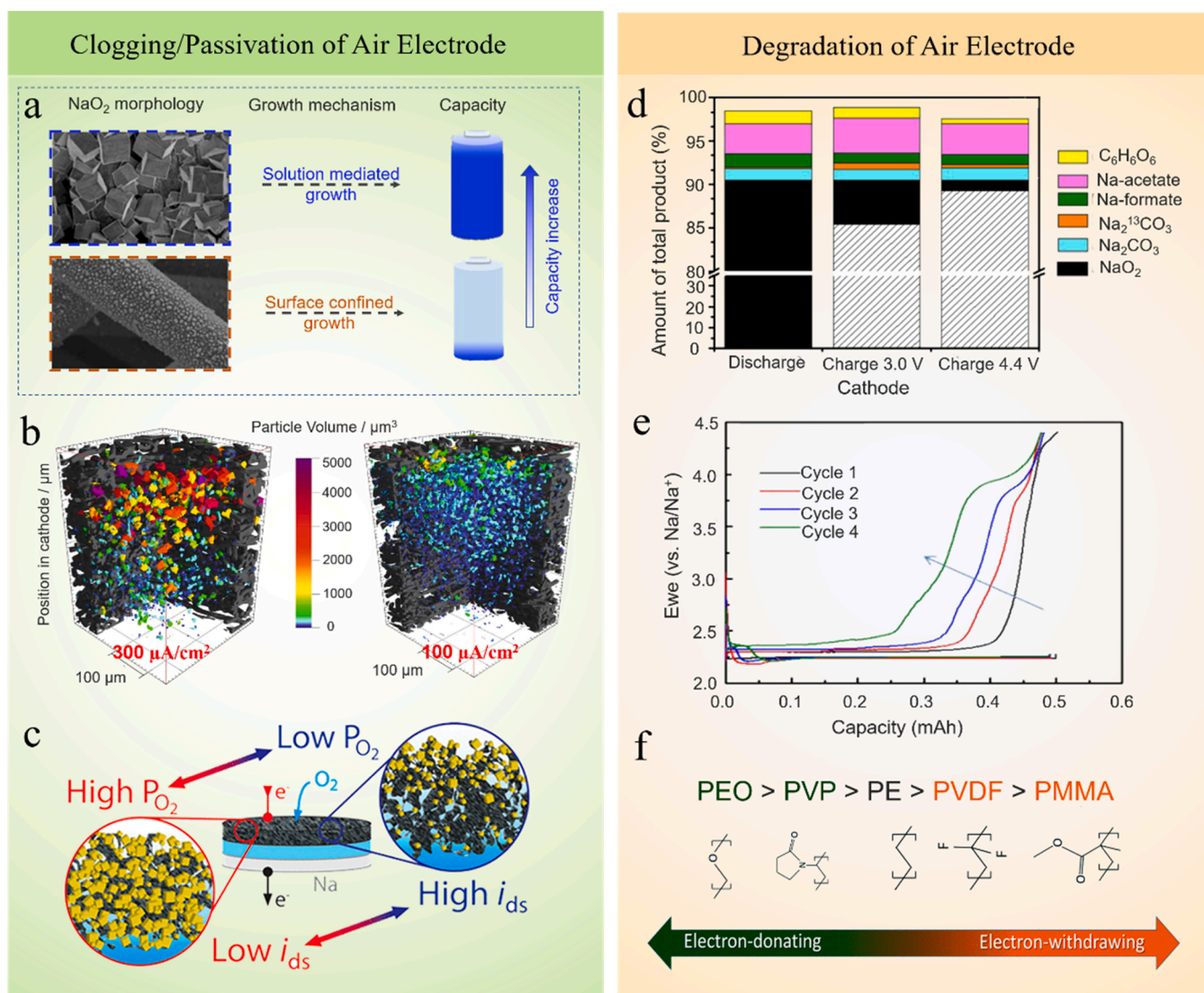


Fig. 7. The issues of air electrodes that affecting the discharge capacity and cycling performance of Na-O₂ batteries. (a) Schematic of the effect of the NaO₂ morphologies on battery capacities via different growth mechanisms [60]; (b) Particle size distribution analysis inside the air electrodes [40]; (c) The influence of oxygen pressure on the formation of NaO₂ [93]; (d) Products as a fraction of the total theoretical product at different stages of cell operation, and (e) working electrode potential of a Na-O₂ cell using a ¹³C cathode with an upper potential limit of 4.4 V [78]; (f) The strength of the electron donating and electron withdrawing groups for different polymer binders [95].

effects of electrons and O₂ mass transport, resulting in the dramatic difference in the spatial NaO₂ distribution at different O₂ pressures.

Compared to the film-like NaO₂, it is widely accepted that the formation of large NaO₂ cubes without cathode clogging is more favorable since it supports a higher utilization of air electrodes. Therefore, the rational design of the air electrode microstructure and optimization of discharge parameters is highly important for enhancing the discharge capacity of Na-O₂ batteries.

3.3.2. Degradation of air electrodes

Carbon-based materials have been widely used as cathode materials in Na-O₂ batteries. However, many critical challenges remain concerning the stability of carbon cathodes against NaO₂, causing structure degradation and poor cycling performance of Na-O₂ batteries.

Great efforts have been made to explore the corrosion mechanisms of carbon cathodes in the Na-O₂ battery system. A discharge experiment using a ¹³C-labeled electrode with released CO₂ isotopes has been conducted by Tarascon and coworkers and in their work, the presence of ¹³CO₂ and ¹²CO₂ indicates the decomposition of both the carbon

cathode and electrolyte, respectively [50]. In another study, Nazar and coworkers performed a solid-state NMR measurement on a ¹³C-labelled cathode at different stages of Na-O₂ cell operation. The ¹³C NMR spectrum of the discharged cathode unambiguously reveals that the formation of Na₂CO₃ by-product is attributed to the oxidation of both the solvent and carbon cathode [78]. As shown in Fig. 7d, the amount of Na₂¹³CO₃ is about three times higher than that of the discharged cathode after recharging to 3.0 V, indicating that the direct oxidation of carbon with NaO₂ can be promoted with a very low charge overpotential. Moreover, charging a cell to the voltage necessary to remove side products is clearly detrimental to the cycling performance of Na-O₂ batteries (Fig. 7e). Nevertheless, these results are different to that of the Li-O₂ batteries, in which the carbon electrode is relatively stable at < 3.5 V and the observed Li₂CO₃ is widely reported to be as result of electrolyte decomposition rather than direct carbon corrosion [96–98]. Although the Li₂O₂-carbon reaction is thermodynamically favorable, the slow kinetics of the Li₂O₂-carbon reactions may be responsible for these discrepancies in Li- and Na-O₂ battery systems.

More recently, our group proposed that the formation of Na₂CO₃ or

NaHCO_3 is related to the oxidation of the defect sites at the air electrode surface by reactive O_2^- radicals [74]. For air electrodes using polymer binders, their stability is also an issue. The reactivity of NaO_2 with the air electrode (PVDF binder) has been confirmed with the formation of NaF and Na_2CO_3 by using solid-state ^{23}Na NMR spectroscopy [72]. A detailed work which investigates the electrochemical behavior of cathodes with four different polymer binders was conducted by our group in 2017 [95]. We proposed that the existence of electron withdrawing groups (EDGs) in the polymer backbones can result in the activation of $\alpha/\beta\text{-H}$ and increased acidity, which is responsible for the instability of polymer binders against $\text{O}_2/\text{O}_2^{2-}$ as well as the increase in side reactions in Na-O_2 batteries (Fig. 7f). It is important to note that the decomposition of polymer binders may damage the integrity of the air electrodes and lead to concerns regarding electron transport. On the other hand, the insoluble by-products which arise from carbon cathode degradation progressively covers the electrode active sites and thus impedes the ORR process, which is a major reason for premature Na-O_2 cell failure. Therefore, more attention should be paid to alleviate undesirable carbon cathode passivation when designing the air electrode for Na-O_2 batteries.

3.3.3. Rational design of O_2 -breathing air electrode

Increasing the specific capacity and power capability of Na-O_2 batteries strongly depends on the properties of the air electrode. Apart from general properties such as good electronic conductivity and high structure affinity, the surface chemistry of the air electrodes should be capable of facilitating the reversible formation and decomposition of large NaO_2 cubes. Furthermore, a highly efficient air electrode should possess a hierarchical wide-open porous structure for effective O_2 and Na^+ diffusion, in order to achieve the high utilization of air electrodes. Free-standing air electrodes should also minimize the detrimental side reactions involving polymer binders. Considering the effect of defects, functional groups, and solid catalysts in promoting peroxide formation and carbon cathode/electrolyte degradation, here, we will mainly focus on the microstructure design of pristine carbon cathodes and their effectiveness on alleviating the pore clogging issue.

Various pristine carbon materials have been explored as cathode nanomaterials in Na-O_2 batteries, including carbon black, meso/microporous carbon, carbon nanotubes, and carbon fibers [23,57,99–101]. However, the achievable discharge capacities of Na-O_2 cells differs greatly depending on the type of carbon cathode used, even under the same experimental conditions (Fig. 8a) [23]. This phenomenon is

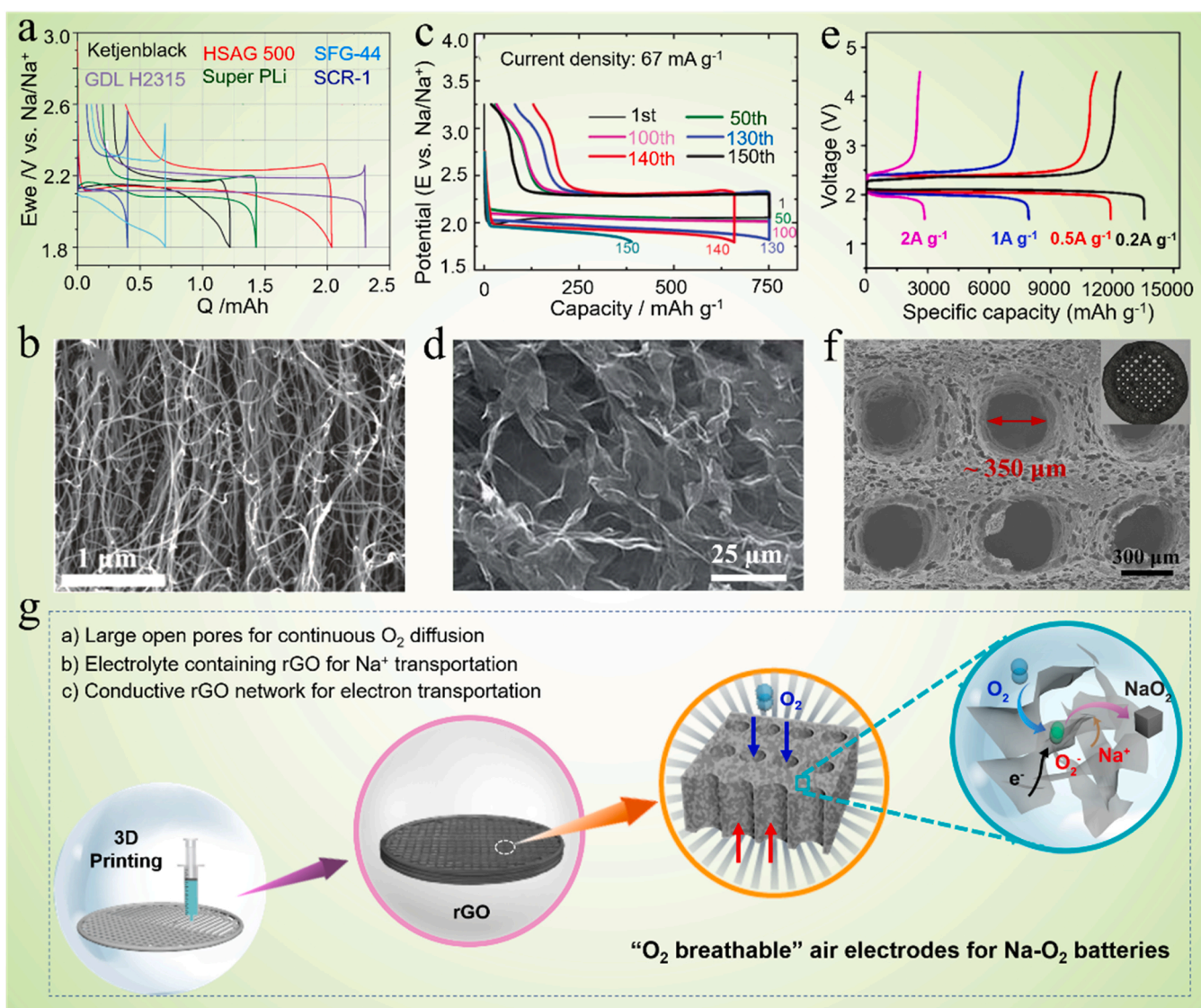


Fig. 8. Rational design of air electrode structures for Na-O_2 batteries. (a) discharge/charge profiles of Na-O_2 cells using air electrodes with different microstructures [23]; (b) SEM image of VACNT cathode, and (c) the cycling performance of Na-O_2 battery with VACNT cathodes [39]; (d) SEM image of the reduced graphene aerogel cathode [103]; (e) Rate performance, (f) SEM image, and (g) schematic illustration of the 3D printed "O₂-breathable" air electrodes for Na-O_2 batteries [104].

related to the microstructure of the air electrodes, which greatly affects the amount of NaO_2 that deposits in the cavity or voids of the cathode. Generally, air electrodes with larger macropores can accommodate more NaO_2 cubes during the discharge process, while pores with smaller size are easily blocked which results in limited capacity. Structural optimization of the air electrodes can induce pronounced enhancements for cell performance. As proved by Sun et al., novel self-stacked nitrogen-doped carbon nanotube (NCNT) electrodes exhibit superior electrochemical performance, due to rapid O_2 and Na^+ transportation as a result of a robust network woven by the aligned NCNT units [102]. Long-term stable cycling of Na- O_2 batteries has also been achieved by using vertically aligned carbon nanotubes (VACNTs) as the air electrode (Fig. 8b and c) [39]. The high surface area of the VACNT cathode provides sufficient active reaction sites and enables more nucleation sites for NaO_2 deposition upon discharge. The electrochemical performance of graphene aerogel cathodes can also be tuned by tailoring the porosity and nanostructure of the cathodes. As reported by Enterria et al., graphene aerogel cathodes with high meso-macroporosity and a narrow macropore size arrangement exhibits the best performance among all studied materials, attributing to faster O_2 diffusion and ORR/OER kinetics within the air electrodes (Fig. 8d) [103]. All these results indicate that increasing the O_2 permeability and surface area of air electrodes are beneficial to enhancing Na- O_2 cell performance.

O_2 gas and the electrolyte (Na^+) often competes for transport pathways in conventional air electrodes, thus, developing novel air electrodes with decoupled O_2 and electrolyte pathways is crucial for achieving high-performance Na- O_2 batteries. Recently, our group fabricated novel “ O_2 breathable” air electrodes by a 3D printing technique for Na- O_2 batteries [104]. The designed air electrode has a stacked mesh structure with macroscale open pores and conductive filaments based on reduced graphene oxide (rGO) sheets (Fig. 8e-g). Excellent rate performance can be achieved for Na- O_2 cells with 3D printed air electrodes, attributing to the unique electrode structure that can provide non-competitive pathways for electrons, O_2 , and the electrolyte. Moreover, the binder-free feature of the air electrodes eliminates parasitic reactions that are induced by proton abstraction of O_2^- from the binder polymer backbone. For the same purpose, different air electrodes with separated charge/mass (O_2 and Na^+) transfer pathways have also been reported in the Li- O_2 battery system, exhibiting excellent electrochemical performance [105–107]. The design of air electrodes with continuous individual pathways for Na^+ ions, O_2 , and electrons opens new opportunities for developing high-capacity and long-life Na- O_2 batteries. Other energy storage systems, such as Li- CO_2 , Na- CO_2 , K- O_2 batteries, which involve reactions on multiple phases can also take inspiration from designing gas breathable cathodes.

3.4. Electrolytes

The electrolyte has a profound influence on the electrochemistry and performance of Na- O_2 batteries. Various non-aqueous electrolytes have been studied for decades and successfully employed in Na-ion cells. However, these electrolytes cannot be directly used in Na- O_2 batteries, due to the unique working mechanism of the system. This is the major reason why Na- O_2 batteries are more challenging to work with. Although a truly stable electrolyte has yet to be demonstrated, ether-based electrolytes have been the prevailing choice for non-aqueous Na- O_2 batteries. In addition to ether-based electrolytes, there have also been cell designs based on dimethyl sulfoxide (DMSO), ether/ionic liquid (IL) hybrid electrolyte, and SSEs. In this section, we divide our discussion into two categories: (1) liquid electrolytes and (2) SSEs. The scientific understanding on the design of solid-state Na- O_2 batteries will also be briefly touched upon in this section.

3.4.1. Liquid electrolytes

An ideal non-aqueous electrolyte for Na- O_2 batteries should have high electrochemical/chemical stability in the presence of reactive

oxygen species, high O_2 solubility and diffusivity, as well as low volatility to guarantee long-term operation. The first requirement is the prerequisites of electrolyte for NaO_2 formation/stabilization in Na- O_2 batteries, and the other two are benefits to enhance the electrochemical performance of Na- O_2 batteries.

Glyme solvents are considered the best compromise for an active Na- O_2 battery system, due to their great resistance to nucleophilic attack and higher cathodic stability [29]. Based on the reports regarding Li- O_2 batteries, the type of glyme solvent can dramatically alter the duration of cell cycling (Fig. 9a). For instance, shorter glymes have shown to be more stable against oxygen species, which is associated with the nature of the active sites on ether molecules [108]. Despite this, NaO_2 has been identified as the major discharge product in Na- O_2 batteries using different glymes including monoglyme (DME), diglyme (DEGDME), and tetraglyme (TEGDME) [60]. On the other hand, glymes with different chain lengths have an impact on the Na- O_2 cell capacities. Short chain solvents tend to deliver high capacities by facilitating large NaO_2 formation via the solution-mediated pathway, attributing to their low chelation effect. With computational simulations validated by FTIR and NMR, Ke et al. further claimed that the utility of short chain solvents for Na- O_2 batteries in specific is linked to their favoring ion association, while the poor performance of long chain ethers in Na- O_2 cells is a result of their excessive binding to sodium [114]. Accordingly, DME should exhibit better electrochemical performance than other glyme solvents. However, it is worth noting that the DME evaporates rapidly during O_2 purge and cell operation due to its high volatility, which is detrimental to long-term cell cycling. Therefore, DEGDME is found to show the best balance between the stability and boiling point, thus is considered the first option for glyme solvents in Na- O_2 batteries.

In ether-based electrolytes, the choice of sodium salts have a significant effect on Na- O_2 cell performance, which works by affecting the stability of the solid electrolyte interphase (SEI) formed on the Na anode (Fig. 9b and c) [109]. Besides, tailoring the salt concentration in ether electrolytes renders NaO_2 with different properties. As reported by Aetukuri et al., there is a strong correlation between the electrolyte salt concentration and NaO_2 crystal size [115]. Based on both theoretical and experimental results, they proposed that the correlation is a direct manifestation of cation-anion pairing interactions, which decreases the growth kinetics and crystal size of NaO_2 due to strong ion pairings at high salt concentrations. In another report, Park et al. successfully demonstrated that the NaO_2 stored in a concentrated ethereal electrolyte exhibits far greater stability and prolonged lifetime in comparison to conventional electrolytes, benefiting from the decreased interactions between NaO_2 and free solvents in concentrated electrolytes [116]. The enhanced NaO_2 stability promises a high energy efficiency and reversibility of Na- O_2 batteries. However, it should be noted that the electrolyte viscosity increases significantly with an increasing salt concentration, which may have an adverse effect on O_2 diffusion during the ORR process, especially at high rates.

DMSO is another attractive solvent candidate for Na- O_2 batteries due to its high polarity, high O_2 solubility, and high chemical stability against reactive species. However, due to the high reactivity of DMSO towards metallic Na anode, its application in Na- O_2 batteries is limited [117]. Based on the DN map of superoxide stability shown in Fig. 9d, the high DN couple of $\text{CF}_3\text{SO}_3^-/\text{DMSO}$ is a promising electrolyte for the reversible operation of Na- O_2 batteries since they are expected to stabilize the superoxide [110]. In terms of reversibility, the Na- O_2 cells based on the $\text{CF}_3\text{SO}_3^-/\text{DMSO}$ couple is superior to even those based on the widely used $\text{CF}_3\text{SO}_3^-/\text{DEGDME}$ pair. To stabilize the Na anode, He and colleagues employed the concentrated NaTFSI/DMSO electrolyte ($> 3 \text{ mol kg}^{-1}$) in Na- O_2 batteries [118]. NaO_2 is identified as the sole discharge product in their report, and more importantly, the cycle life of Na- O_2 batteries is significantly prolonged. Along with electrolyte management, replacing the metallic Na anode with alternatives is another promising approach to eliminate Na-related issues in DMSO-based Na- O_2 batteries [110].

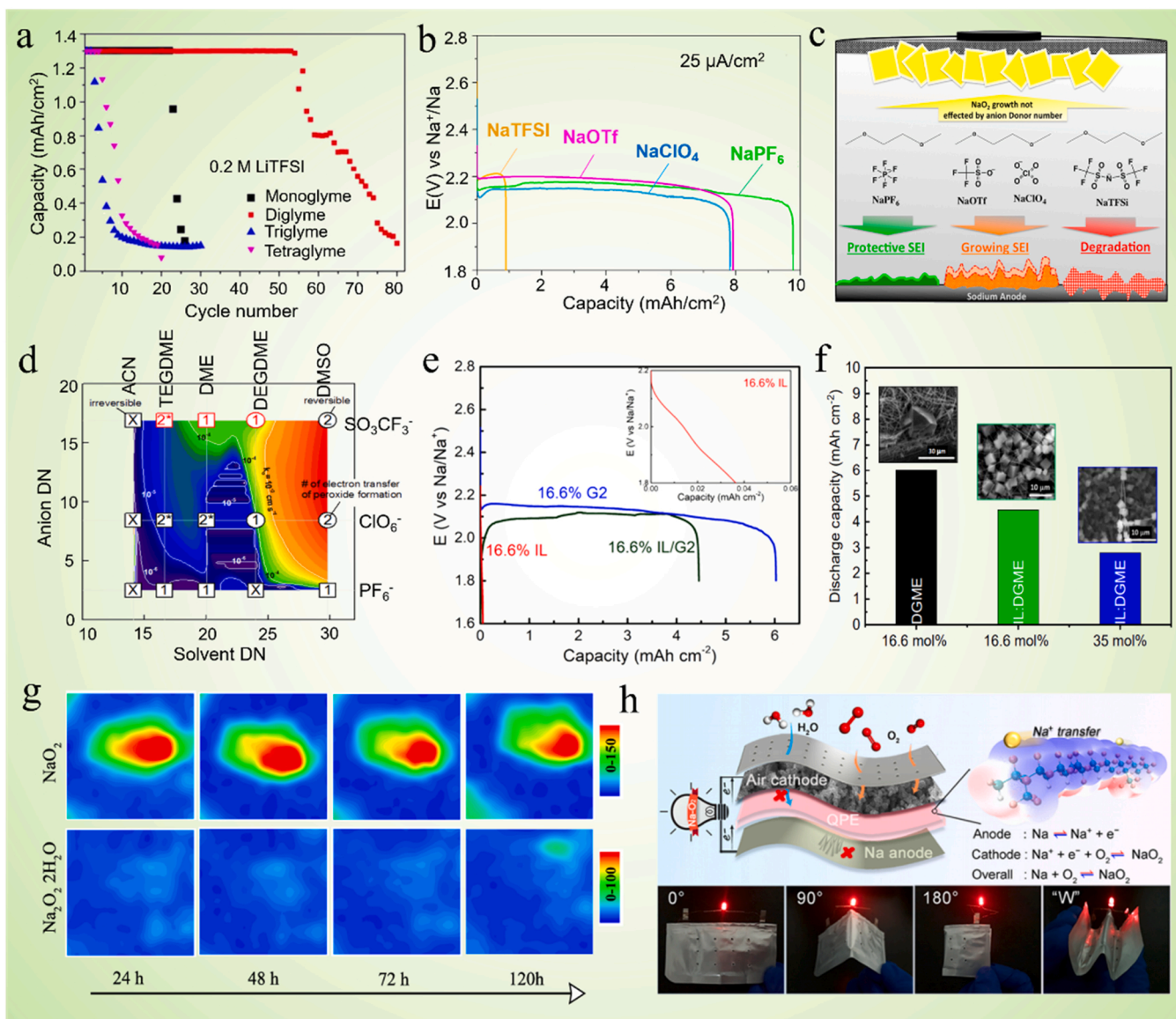


Fig. 9. (a) Cycling behavior of Li-O₂ cells in different glymes containing 0.2 M LiTFSI [108]; (b) Discharge/charge profiles of Na-O₂ cells using 0.5 M DME electrolytes with different salts, and (c) illustration of the SEI formation mechanisms in different DME electrolytes [109]; (d) Contour plots of the standard rate constants (k_o) of superoxide formation on 2D DN map for superoxide stability [110]; (e) Discharge curves of Na-O₂ cells with different electrolytes [111]; (f) Column graph representing the discharge capacity of Na-O₂ cells with different electrolytes along with the corresponding air cathode micrographs [112]; (g) Chemical maps of NaO₂ and Na₂O₂·2 H₂O reproduced from Raman spectra recorded from a NaO₂ cube on the SSE at different time intervals; and (h) Schematic diagram of a Na-O₂ battery using QPE and the optical images of the integrated flexible Na-O₂ battery at different states [113].

The feasibility of ILs in Na-O₂ batteries was also studied due to their high ionic conductivity, low volatility, nonflammability, and stable Na⁺/Na electrochemistry [29,112,119,120]. Among various ILs, N-butyl-N-methyl pyrrolidinium bis(trifluoromethylsulfonyl)imide ([C₄mpyr][TFSI]) is the most studied IL electrolyte, which exhibits a single electron reversible reaction (O₂/O₂⁻) during the ORR process [121]. However, its high viscosity and limited O₂ solubility/diffusivity greatly restricts Na-O₂ cell performance [122]. In 2020, Ortiz-Vitoriano and co-workers proposed a concept of a glyme/IL hybrid electrolyte, in which the IL act as a fire retardant while the glyme increases the Na⁺ mobility. Despite the relatively lower cell capacity compared to a pure glyme electrolyte, the synergistic effects of diglyme and IL solvents can enhance the stability of O₂ intermediates, benefiting to the decrease of parasitic reactions and homogeneous NaO₂ growth (Fig. 9e) [111]. On the other hand, they found that stronger coordination of Na⁺ by DEGDME in the less concentrated hybrid electrolyte (16.6 mol% NaTFSI) leads to fewer nucleation sites and larger NaO₂ formation than

that of the 35 mol%-based hybrid electrolyte (Fig. 9f) [112].

3.4.2. Solid-state electrolytes

Compared with organic liquid electrolytes, SSEs can enhance the safety of Na-O₂ batteries by suppressing Na dendrite growth and avoiding electrolyte evaporation/leakage. Another advantage of the SSE is the inhibition of contaminant crossover from the cathode to the anode, preventing corrosion of the metallic Na anode during cell operation [56]. An ideal SSE for solid-state Na-O₂ batteries must have high ionic conductivity, good air stability, a wide electrochemical stability window, as well as good chemical stability against the attack of reduced reactive species produced during cell operation. Considering the practical application of solid-state Na-O₂ batteries in the future, simple processability, cost-effectiveness, and environmental friendliness of SSEs are also important. So far, significant progress has been achieved in developing various solid-state Na-ion conductors including organic (polymer) and inorganic (oxides, sulfides, and halides) SSEs [123].

Although sulfide electrolytes features high ionic conductivity and good deformability, their air (moisture) sensitivity and narrow electrochemical stability window severely inhibit their feasibility in Na-O₂ batteries. Recently reviving halide SSEs are attractive due to their high-voltage stability, moderate mechanical property, and cost-effectiveness. However, their stability during long-term Na-O₂ cell cycling remains unclear and more investigation is needed in the future study. So far, the development of solid-state Na-O₂ cells is at the initial stage due to the short history of Na-O₂ technology, and the main SSEs developed for solid-state Na-O₂ batteries are oxides- and polymer-based SSEs [56,69,113].

Oxide-based SSEs possess good air stability and high ionic conductivity, while their high elastic modulus nature limit their application as a single-component SSE in Na-O₂ cells. Generally, oxide SSEs are coupled with liquid electrolytes or ionic liquids to construct hybrid-solid-state Na-O₂ batteries. In 2013, Na-β''-Al₂O₃ was introduced into Na-O₂ battery system as a solid electrolyte membrane by Hartmann et al., which is effective in suppressing the Na dendrite growth [69]. When coupling Na-β''-Al₂O₃ electrolyte and nanoporous gold film cathode in a Na-O₂ battery, the cells were reversibly cycled at a relatively low overpotential of ~450 mV with Na₂O₂ as the main discharge product. Hybrid solid-state Na-O₂ batteries based on NASICON-type Na_{3.25}Zr₂Si_{2.25}P_{0.75}O₁₂ SSE were first reported by our group [56]. The introduction of NASICON SSE do not alter the ORR pathway, and one-electron transfer with NaO₂ as only discharge product was observed. Further, the Na_{3.25}Zr₂Si_{2.25}P_{0.75}O₁₂ SSE is proven to be chemically stable against the NaO₂ and superoxide radicals (Fig. 9g). More importantly, it was revealed that the SSE can act as a shield to eliminate the detrimental effect of O₂/O₂⁻ crossover, which significantly enhances the cycling stability of the Na anode in Na-O₂ batteries.

More recently, flexible gel polymer electrolytes have been tested in Na-O₂ batteries. For example, Wang et al. designed a quasi-solid-state polymer electrolyte (QPE) that consists of poly(vinylidene fluoride-co-hexafluoropropylene)–4% SiO₂-NaClO₄-TEGDME (Fig. 9h) [113]. The QPE exhibits the merits of high ionic conductivity, nonflammability, hydrophobicity, and at the same time, enables the homogeneous deposition of Na deposition. The constructed quasi-solid-state (QSS) Na-O₂ batteries can run stably for over 80 cycles under a shallow cycling mode, with an average coulombic efficiency of >97%. Moreover, flexible pouch-type Na-O₂ batteries show stable electrochemical performance

for ~400 h at various bending or folding states (0–360°). Despite this, the cycle life of QSS Na-O₂ batteries is still far from satisfactory, and further investigations of solid-state Na-O₂ batteries with high safety and enhanced performance acceptable for practical application are required.

3.5. Na metal anode

To maximize the potential of Na-O₂ batteries, Na metal is considered the best choice for the negative electrode, due to its high specific capacity, low electrochemical equilibrium potential, and earth-abundant nature. However, the practical electrochemical performance of Na-O₂ batteries is proving to be severely limited, due to issues stemming from the Na metal anode. To realize the practical application of Na-O₂ batteries, more attention should be given to Na metal protection. In this section, we first describe common issues faced by using a metallic Na anode in Na-O₂ batteries and their underlying reasons. Then, representative and effective strategies that can help realize efficient use of the Na metal anode will be presented.

3.5.1. The challenges of metallic Na anode

As shown in Fig. 10, the major challenges of the metallic Na anode in Na-O₂ batteries can be classified as follows: uncontrolled interfacial parasitic reactions, unstable SEI layer, and harmful Na dendrite growth. The organic electrolyte can be readily reduced by the highly reactive Na metal, resulting in the formation of a SEI layer that is comprised of reduction products of the electrolyte on the Na surface. The ideal SEI layer should be electronically insulating but ionically conductive and exhibit high mechanical strength. Furthermore, the SEI should uniformly cover the Na anode. Nevertheless, in practical batteries, the actual SEI film cannot fully exhibit all these properties. The spontaneously formed SEI layer on Na is typically incompact and vulnerable to cracking, which exposes more Na to continuous and undesirable side reactions [109,124,125].

Impurities or additives in the electrolyte can result in the occurrence of parasitic reactions on the Na anode surface. For example, a water additive in the electrolyte acts as the PPTC on the cathode and can directly react with Na anode to form NaOH [37]. CO₂ and H₂O contaminants that arise from electrolyte decomposition and cathode degradation also have detrimental effects on the Na metal anodes performance by direct reactions [9]. Furthermore, due to the unique

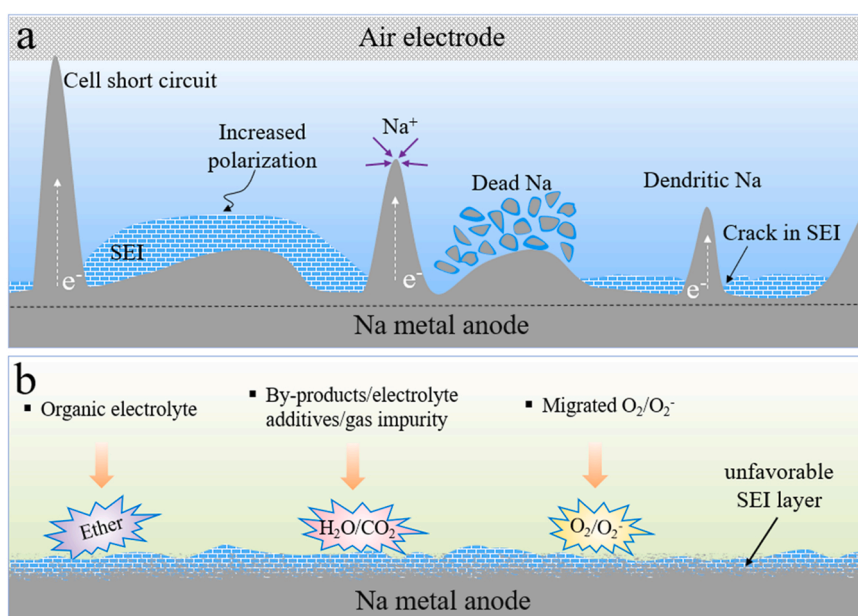


Fig. 10. The issues of Na metal anodes in Na-O₂ batteries. (a) Illustration of detrimental effects of Na dendrites during cell operation; (b) the schematic of unfavorable SEI layer formed on the Na anode surface via various chemical/electrochemical reactions.

reaction mechanism of superoxide-based Na-O₂ batteries, the parasitic reactions that are induced by dissolved oxygen species including O₂ and O₂⁻ on the Na surface should also be taken into consideration, which is discussed in detail in the Section 3.6. Undoubtedly, the continuous parasitic reactions on the Na anode will result in the gradual growth of a SEI on the Na surface, a sharp increase in polarization, and premature Na-O₂ cell failure.

Na dendrite growth has also been experimentally proven to be a formidable challenge for safe and long-term cycling of Na-O₂ batteries [19,39,126,127]. According to previous studies on Na-ion batteries, Na dendrites originate from the inhomogeneous distribution of electrons on the rough Na surface and/or the concentration gradient of Na⁺ at the SEI layer. The growth of dendritic Na leads to cracking and collapse of the fragile SEI layer, which can in return exacerbate Na dendrite growth. Moreover, during the stripping process, the Na dendrites can detach from the bulk Na to form “dead Na”, due to dissolution of Na near the base of the Na dendrite. Along with the loss of active materials, the formation of “dead Na” is extremely problematic due to its chemically hyper-reactive nature as a result of high surface area. More importantly, Na dendrites can cause internal short circuits in the cell and lead to dangerous fires and explosions after penetrating the separator. Na dendrite growth is a common issue of Na-based batteries, and the growth mechanism of Na dendrites has been extensively studied in Na-ion batteries. However, Na dendrites may exhibit distinct growth mechanisms in Na-O₂ batteries, as superoxide are involved during cell operation. Therefore, further investigation is needed to have an in-depth and comprehensive understanding on the Na anode in Na-O₂ batteries.

3.5.2. Strategies to stabilize Na metal anode

Considering the severe parasitic reactions at the Na anode and harmful Na dendrite growth, developing strategies to stabilize the Na metal anode is crucial for addressing safety hazards and poor Na-O₂ cell performance. Different to Na-ion cells, Na anode protection in Na-O₂ batteries is more complicated, due to the unique reaction mechanisms of the system. Thus, strategies for Na-ion batteries do not necessarily achieve the same efficiency in Na-O₂ batteries. To date, a considerable number of strategies have been proposed to resolve the Na issues in Na

metal batteries, and stable cycling of the Na anode in Na-O₂ batteries has also achieved modest success. In this section, we briefly review the protection mechanisms, promising strategies, and special considerations that required in terms of Na protection for the Na-O₂ battery system.

First, electrolyte management is one of the most effective ways to facilitate stable Na cycling, since the nature of the SEI layer is dominated by the properties of the organic electrolyte. Optimizing salt-solvent combinations or adding suitable electrolyte additives can promote the formation of uniform and robust SEI layers that are enriched in inorganic components, owing to the Na interfacial stability by insulating Na metal from electrolyte penetration and inhibiting the dendrite penetration due to their high shear modulus (Fig. 11a) [109,124,125,128,129]. There have also been reports of stabilizing the Na anode by adding the trace bi-functional electrolyte additive potassium bis(trifluoromethylsulfonyl)imide (KTFSI), where TFSI anions decompose into lithium nitride and oxynitrides to render a desirable SEI layer, while the K⁺ cations accumulate surrounding the Na tip and provide electrostatic shielding to suppress Na dendrite growth (Fig. 11b) [130]. The electrostatic shield mechanism of K⁺ in the electrolyte is identical to that of Cs⁺ reported on Li metal protection [130]. Increasing the salt concentration in the electrolyte can change the solution structure and renders electrolytes with many unique properties [118,131,132]. For example, the Na cycling stability can be significantly improved in a DMSO electrolyte with concentrated NaTFSI salts [118]. The enhanced Na stability correlates with the reduced amount of free DMSO molecules that are susceptible to the Na attack and renders TFSI anion decomposition, leading to the formation of a protected surface layer.

Second, constructing a stable and robust artificial SEI layer via surface engineering is a facile method to suppress dendrite formation and prevent severe Na corrosion. Crystalline NaBr coatings on the Na anode surface were successfully fabricated by Choudhury et al. by directly exposing Na metal to 1-bromopropane liquid (Fig. 11c) [133]. The protective Bi layer has also been fabricated through a deliberate reaction between the Na metal anode and Bi(SO₃CF₃)₃ in an ether solvent, achieving improved electrochemical stability and cycling life in Na-O₂ batteries [138]. The solution-based surface chemistry route is a simple and efficient way to introduce an artificial SEI layer on the Na anode,

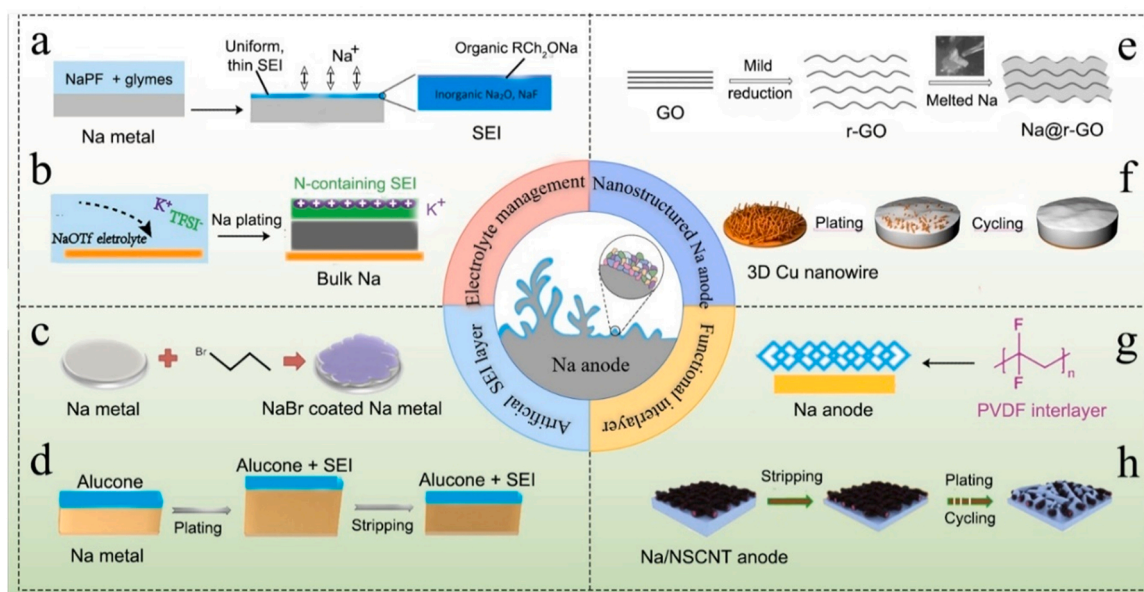


Fig. 11. Strategies for fabricating stable Na metal anodes. (a) Schematic showing the SEI layer formed on the Na anode surface by adding NaPF₆ in glyme electrolytes [124]; (b) Schematics showing the stabilization effects of KTFSI salt for Na metal deposition [130]; (c) Schematic showing the procedure to introduce artificial NaBr layer on Na anode [133]; (d) Schematic diagram of Na stripping/plating on Na anode with artificial alucone protective layer [134]; (e) Schematic representation of the preparation of Na@r-GO composite anode [135]; (f) Schematic illustration of Na plating and cycling on 3D current collector with Cu nanowires [136]; (g) Schematic of the Na anode design with *t*-PVDF blocking interlayer [137]; (h) Schematic illustration of the Na stripping/plating on Na/NSCNT anode [127].

however uniform coatings with controllable thickness remains challenging. Atomic/molecular layer deposition (ALD/MLD) is recognized as a novel coating technique, as it can enable conformal coatings on various substrates with well-controlled thickness. To date, metal oxides and organic-inorganic films have been successfully deposited by ALD/MLD, demonstrating their feasible use in stabilizing Li/Na electrodes in symmetric cells (Fig. 11d) [134,139–141]. While considering the crossover of corrosive species (O_2 , O_2^- , 1O_2) from the cathode to the Na anode, the feasibility of organic and organic-inorganic artificial SEI films in the Na- O_2 battery system needs further investigation.

To facilitate uniform Na^+ flux and prevent dendrite formation, researchers have tried to design various composite Na anodes by using 3D host materials with pre-stored Na or 3D current collectors with electrochemically deposited Na. Luo's group reported a Na-reduced graphene oxide (Na-rGO) composite electrode by pre-storing metallic Na into a GO film via thermal infusion (Fig. 11e) [135]. The rGO sheets in the composite electrode produced a uniformly distributed Na^+ flux, and at the same time, the composite anode exhibited enhanced stability against corrosion by preventing the direct contact between Na and the electrolyte. These characteristics of the Na-rGO electrode benefit to the homogeneous plating of Na in Na- O_2 batteries. A series of 3D host matrices were developed in Na-ion batteries, and have achieved exciting improvements regarding Na anode performance [142–144]. 3D porous Al and Cu foils were reported as the current collector to suppress the Na dendrites (Fig. 11f) [145,146]. The high surface area of the 3D current collectors can reduce the local current density and provide more electrodeposition sites for Na^+ , enabling homogeneous Na plating. These approaches can be transferable from the Na metal batteries to Na- O_2 batteries in terms of Na dendrite suppression, while the undesired parasitic reactions induced by migrated corrosive species (O_2 , O_2^- , 1O_2) cannot be effectively impeded in Na- O_2 batteries.

Finally, introducing a functional interlayer on the Na anode surface has also shown to be a promising strategy to enhance Na- O_2 cell performance. A non-conductive polyvinylidene fluoride fiber film (f-PVDF) with nonthought pore is proposed as a blocking interlayer by Ma's group, and the enhanced Na- O_2 cell performance is attributed to the strong affinity of the C-F polar function groups to Na ions that enables homogeneous Na deposition (Fig. 11g) [137]. The strategy of incorporating conductive interlayers in Na- O_2 batteries have been separately reported by Wang's group and our group [19,127]. Wang's group used nitrogen and sulfur co-doped carbon nanotube (NSCNT) paper to demonstrate their ability to efficiently stabilize the Na metal anode (Fig. 11h) [127]. The high surface area of NSCNT can decrease the local current density and the "sodiophilic" functional groups on NSCNT can effectively guide the initial Na nucleation, synergistically contributing to uniform Na plating without dendrite formation. More interestingly, apart from the suppression of dendrites, we found that the conductive interlayer maintains a pseudo-equal potential with the Na metal and functions as a protective layer to alleviate Na degradation induced by O_2/O_2^- crossover, which greatly enhances the reversibility and cycle life of Na- O_2 batteries [19]. Currently, Na degradation induced by contaminant crossover has only been alleviated by porous interlayers rather than completely inhibited, thus it is important to develop new strategies that can completely block contaminant crossover from the cathode to the anode.

3.6. Oxygen and superoxide crossover from air electrode to anode

For superoxide-based Na- O_2 batteries, intractable problems also exist in relation to O_2/O_2^- crossover from the cathode to the anode. On one hand, the O_2^- crossover causes the loss of reversible charge capacity due to the consumption of O_2^- intermediates on the anode side. More concerning however is that the metallic Na anode experiences attack by migrated O_2/O_2^- radicals, which makes the Na-related scenario more complicated. The O_2/O_2^- crossover issue has received underwhelming attention, thus effective strategies to block contaminant crossover are

highly desired for enhancing Na- O_2 battery performance.

3.6.1. Corrosion of Na by the migrated O_2/O_2^-

Na corrosion induced by O_2/O_2^- crossover is an inevitable factor which degrades Na- O_2 battery performance and should not be ignored. O_2^- crossover is a common challenge faced by metal- O_2 batteries including Li, Na-, and K- O_2 batteries [147–150]. However, in Na- O_2 batteries, the solution-mediated pathway for NaO_2 formation results in the formation of dissolved O_2^- intermediates. After intensive investigation, our group firstly pointed out that under the dual effects of a concentration gradient and electric field, the dissolved O_2^- radicals at the cathode can diffuse/migrate to the Na anodes [19]. The O_2^- radicals is a strong oxidant and an initiator of radical reactions, which makes the Na metal anode more vulnerable to being attacked. To clarify the degradation mechanism of the Na anode in the presence of O_2/O_2^- crossover, the nature of the SEI layer on the Na anodes were characterized by employing X-ray photoelectron spectroscopy (XPS) with depth profiling [56]. Electrolyte decomposition and subsequent formation of various by-products on the Na surface can be clearly observed, which indicates that the Na anodes can severely corrode due to complex side reactions involving migrated O_2 and/or O_2^- (Fig. 12). Moreover, the presence of organic reduction products throughout the anode SEI layer contributes to a loose SEI structure that is permeable to O_2/O_2^- and the electrolyte, which results in electrolyte decomposition and continuous SEI layer growth during cell operation. Compared to O_2 , the highly reactive O_2^- can induce intensified side reactions, causing varying SEI compositions and thicknesses. It is clear that parasitic reactions on the Na surface are accelerated by O_2 and O_2^- crossover, and Na anode deterioration eventually results in capacity fading and premature death of the Na- O_2 battery.

3.6.2. Strategy to mitigate the O_2/O_2^- crossover effect

Since the crossover effect originates from the migration of O_2/O_2^- from the cathode to the anode, confining the O_2/O_2^- to the cathode side is critical in enhancing Na- O_2 cell performance. In Na- O_2 batteries, replacing the porous GF separator with an ion selective barrier, which is conductive to Na^+ but impermeable to O_2/O_2^- , is a promising approach for addressing the O_2/O_2^- crossover problem. A NASICON-type SSE was demonstrated by our group as an ideal shield to block oxygen species migration (Fig. 12) [56]. By mitigating the loss of O_2^- intermediates, the hybrid Na- O_2 batteries can be recharged with enhanced coulombic efficiencies. Additionally, stable cycling can be maintained for over 160 cycles with no obvious overpotential increase, demonstrating the effectiveness of the SSE in preventing Na degradation and stabilizing SEI layer. Along with the NASICON-type SSE, other O_2/O_2^- crossover inhibitors including a Nafion- Na^+ membrane, ceramic β'' -alumina solid electrolyte membrane, and mechanically reinforced membrane have also been reported [69,150,151].

The O_2/O_2^- crossover challenge has only been acknowledged in recent years, thus there are very few studies which focus on this problem. In contrast, there are numerous strategies which have been developed to prevent the shuttling of polysulfides in Li-S batteries. For example, metal organic framework (MOF) based separators have been developed as a ionic sieve for Li-S batteries, since the pore size of the MOF is similar to the size of polysulfides [146]. Oxygen electronegative atoms modified GO membrane can also act as a cationic selective membrane, which allows ion hooping of positive charge species (Li^+) but rejects the transportation of anions (polysulfide anions) due to the electrostatic interactions, and the shuttle of polysulfide can be greatly suppressed [152]. Modified separators performing dual physical/chemical roles to inhibit the polysulfide shuttle are also reported with ultra-stable Li-S battery performance [153]. Taking inspiration from Li-S batteries, developing functional separators and interlayers to block O_2/O_2^- migration are promising strategies for achieving high performance Na- O_2 batteries.

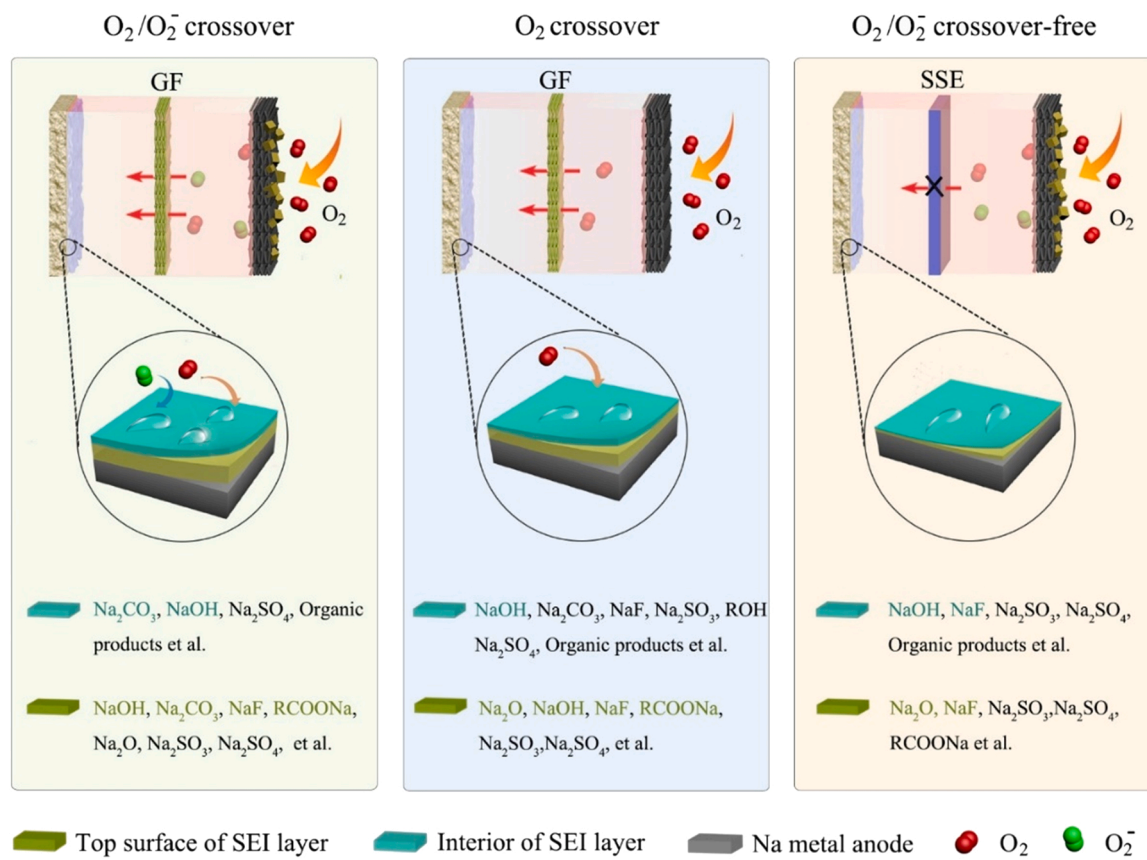


Fig. 12. Schematic illustration of the SEI formation on the Na anode surface under difference conditions. (a) In the presence of O_2/O_2^- crossover, (b) in the presence of O_2 crossover, and (c) in the absence of O_2/O_2^- crossover [56].

4. Conclusion and future perspectives

With the cascading demand for next-generation devices such as high performance EVs and aerial drones, there is a global pursuit to develop novel energy storage devices that can outperform the performance and safety metrics of current LIBs, which currently dominate the battery industry. Among the new battery technologies, Na- O_2 batteries are a promising candidate to replace LIBs as they boast higher energy densities and lower cost. In particular, superoxide-based Na- O_2 batteries have attracted tremendous research interests comparing to other types of metal-air batteries due to their superior energy efficiency. However, the practical application of superoxide-based Na- O_2 batteries is still hindered by their low achievable capacities and poor cycling performance up to now. This review has provided a comprehensive summary of the development of superoxide-based Na- O_2 batteries, including major historical progress, their associated technical issues, and recent progress regarding the air electrode, electrolyte, and the Na anode. Tremendous progresses have been made towards understanding the fundamental electrochemistry and chemistry behind superoxide-based Na- O_2 batteries. It is important to recognize that O_2 reduction towards NaO_2 cube formation can be carefully controlled by tuning the types of electrolyte, air electrode, and operating conditions. The charge behaviors and cycling stability of Na- O_2 batteries are largely dictated by the chemical stability of NaO_2 cubes and the parasitic chemistries involving singlet oxygen and the reduced oxygen species (O_2 , HOO^\cdot , HOO^- , and HO^\cdot). Furthermore, the properties of the air electrode and electrolyte, the stability of Na metal anode, and O_2/O_2^- crossover also play significant roles in Na- O_2 cell performance. Designing novel strategies and discovering ways to integrate them with practical Na- O_2 cells is essential for achieving Na- O_2 batteries with high capacity and long cycle life.

4.1. Deeper understanding on Na- O_2 electrochemistry/chemistry

Superoxide-based Na- O_2 batteries are complex in terms of their reaction mechanism, due to the formation of not only superoxide discharge products but also multiple reactive species as intermediates. A further deepened understanding on the cell electrochemistry will be of great assistance to designing better superoxide-based Na- O_2 batteries. It has been reported that the ORR is highly determined by the properties of cell components and operating conditions, while the factors that govern the reaction paths towards desirable NaO_2 formation in Na- O_2 batteries are not fully understood, thus more fundamental studies will be required. Furthermore, understanding the origin of low charge overpotential after the formation of large insulating NaO_2 cubes is also an important direction for future research.

Parasitic chemistry on the cathode side is considered as one of the major barriers for reversible Na- O_2 cell operation. Thus, more work is needed to investigate the nature of the species which trigger these parasitic reactions. Recent findings have suggested that the main cause of electrolyte degradation is more related to reactive 1O_2 is formed during both the discharge and charge process than NaO_2 and other reduced oxygen species (O_2 , HOO^\cdot , HOO^- , and HO^\cdot). Identifying the factors that influence 1O_2 formation and developing ways to mitigate the detrimental effect of 1O_2 towards Na- O_2 cell performance are important directions of future research. Though the mechanisms of parasitic chemistries involving the reduced oxygen species and 1O_2 have been studied, the possible synergistic effect between these side reactions is still poorly understood and more research is needed.

Adaption of advanced characterization techniques is an effective strategy for the understanding of Na- O_2 electrochemistry/chemistry. Ex-situ analysis on the highly reactive NaO_2 , radical species, and parasitic products in Na- O_2 cells is affected by trace contaminants in the

surrounding environment. In situ/operando techniques which allow the study of the reactions without interference induced by disassembly or a new environment, will help to have a better understanding of the electrochemistry/chemistry involved in Na-O₂ batteries. For example, in situ/operando spectroscopy and microscopy techniques, such as surface enhanced Raman spectroscopy, ultraviolet-visible spectroscopy, scanning electron microscopy, and atomic force microscopy, can probe reaction intermediates, unveil the morphologies of the discharge products, and monitor their morphological/composition evolution during cell cycling, providing further insight into the reaction mechanism and root cause of Na-O₂ cell failure. Monitoring the gas evolution of Na-O₂ cells have been combined with a pressure transducer is important for the deeper understanding of parasitic chemistries. On the other hand, in-situ X-ray tomography and cryo-based techniques are good ways to reveal the mechanism of Na dendrite growth and Na degradation induced by O₂/O₂⁻ crossover during Na-O₂ operation.

4.2. Development of efficient air electrodes

Future efforts should also be directed towards the development of highly efficient air electrodes in order to achieve high-performance Na-O₂ batteries. NaO₂ cube formation via the solution pathway seems to be the desired pathway for achieving high capacities. However, very few designs have realized full utilization of the air electrode due to the clogging of electrode pores by micrometer sized NaO₂. Poor clogging can be avoided by designing air electrode structures with separated channels for O₂ and electrolyte transport, which can also facilitate continuous O₂ transportation, enabling Na-O₂ batteries with high capacity.

Currently, the degradation of carbon-based cathodes remains a pending problem that restricts the cycling stability and cycle life of Na-O₂ batteries. Cathode degradation can be ascribed to the instability of carbon materials and polymer binders against the reactive species. Constructing binder-free air electrodes is a promising strategy to eliminate the parasitic reactions induced by nucleophilic attack of superoxide towards binders. Protection strategies such as surface coatings on the air electrode with highly conductive and stable materials can help boost the chemical stability of the carbon cathode. Additionally, it is worth mentioning that attaching a catalyst on the cathode is effective in facilitating discharge product oxidation with a low charge overpotential. However, possible parasitic reactions induced by the catalyst should be considered when choosing a suitable catalyst in Na-O₂ batteries.

4.3. Development of stable Na anode

The stabilization of the Na metal anode is pivotal for realizing a practical Na-O₂ battery. Due to the unique working mechanism of Na-O₂ batteries involving dissolved superoxide intermediates, the issues regarding the Na anode are far more complicated in comparison to the sodium-ion battery system. The Na anode poses safety concerns and premature cell death due to the growth of Na dendrites during cycling. Furthermore, the reactivity of the Na anode towards organic electrolytes and migrated reactive species (O₂, O₂⁻, ¹O₂) results in Na degradation and Na-O₂ cell performance decay. The Na protection methodologies that have been found to work in sodium-ion batteries can provide some guidance when developing strategies to stabilize the Na anode in Na-O₂ batteries. For example, constructing a 3D Na anode or employing a 3D current collector can effectively suppress Na dendrite growth by reducing the local current density and providing more Na⁺ electrodeposition sites. However, the undesired parasitic reactions induced by migrated corrosive species cannot be effectively deterred when using these methodologies, which impedes long-term stable cycling of the Na anode in Na-O₂ batteries. Surface engineering is typical approach to stabilize the SEI layer and suppress Na dendrite growth in sodium-ion batteries, however, the feasibility of introducing organic and organic-inorganic artificial SEI films on the Na anode in Na-O₂ batteries need

further investigation, the films may be highly vulnerable superoxide attack. Therefore, the strategies used for Na protection in sodium-ion batteries cannot be directly applied to Na-O₂ batteries, thus other approaches to suppress Na dendrite growth and block O₂/O₂⁻ crossover should be explored. Future work should also include a detailed investigation on the Na anode to reveal the root cause of Na degradation, which will help develop effective strategies to stabilize Na anode and the eventual realization of practical Na-O₂ batteries.

In addition to the above-mentioned strategies, new methods to address the Na anode issues in Na-O₂ batteries can benefit from drawing inspiration from other battery systems. There are some methods of Li protection against Li dendrite and O₂/polysulfide crossing in Li-O₂ and Li-S batteries have the potential to be used in protecting Na anode in superoxide-based Na-O₂ batteries: (i) Cathode design. Cathode design is generally be realized by introducing functional groups or adsorbed materials to increase the chemical interaction between dissolved intermediates and the cathode substrates, promising to alleviate the migration of O₂⁻ towards the Na anode. (ii) Separator modification. Functional modification of separator can effectively restrain the crossover/shuttle effect by physical obstruction or chemical bonding of dissolved intermediates. Further, Na⁺ ion selective membrane and solid-state electrolytes are promising candidates to retard the migration of O₂/O₂⁻ in Na-O₂ batteries. (iii) Anode protection. Many novel Li protection methods that have yet to be studied in sodium systems may can provide guidance for the future research of Na anode in Na-O₂ batteries, and should be further explored.

It should be noted that the intercalation-based anode free sodium metal batteries have been reported with considerable research progress, while no reports have been presented for anode free Na-O₂ batteries [154]. The anode-free Na-O₂ battery offers the opportunity to realize maximum utilization of Na anode and to reach a much higher gravimetric/volumetric capacity. In investigating the pathways that controlling the Na₂O₂ formation, Janek's group found that the Na₂O₂ can be removed from the cathodes preloaded with Na₂O₂ during charging, with NaO₂ generated in the subsequent discharge process [20]. Although Na metal was used as the anode material in their design, the success decomposition of Na₂O₂ indicates the feasibility of Na₂O₂ as the cathode of anode-free Na-O₂ batteries. Except for Na₂O₂, cathodes preloaded with Na₂O also shows promising prospect in terms of anode-free cell design. Similarly, when designing anode-free Na-O₂ batteries, attention must be paid to preventing the Na dendrite growth and reducing the negative effects of oxygen/superoxide crossover towards the anode.

4.4. Higher electrochemical performance and safer electrolyte: from liquid to solid

Electrolyte design in superoxide-based Na-O₂ batteries should be a main research priority, as the electrolyte determines the ORR routes and greatly influences cell performance. On screening all the known electrolyte solvents, undesirable side reactions have more or less been found. Therefore, it is highly desirable to discover and design stable organic electrolytes that can tolerate highly oxidizing environments in Na-O₂ batteries.

A promising research direction to avoid the parasitic reactions associated with solvent instability is through the construction of all solid-state Na-O₂ cells. Replacing the flammable organic electrolyte with highly stable SSEs not only can greatly enhance the safety of Na-O₂ battery, but also can enhance the cell performance by preventing oxygen/superoxide crossover. One of the most important criterions for selecting SSE is its compatibility with O₂⁻ radicals and other reactive oxygen species. The representative inorganic Na⁺ ion conductors with high room-temperature ionic conductivities including Na-β''-Al₂O₃ and NASICON have been reported to be highly stable in superoxide-based Na-O₂ [155]. Due to the rigid nature of these electrolytes, addressing the issue of interfacial contacts include Na/solid-state electrolyte and solid-state electrolyte/cathode is critical for the success construction of

all-solid-state Na-O₂ battery.

Designing a highly functional solid-state air electrode is another bottleneck for the further development of solid-state Na-O₂ batteries. The flowing O₂ and discharge product NaO₂ must be interfaced with the electronic conductors and ionic conductors to ensure complete electrochemical cycling. However, these essential interfaces are distributed discontinuously and in the form of point-to-point in solid-state electrodes [156]. Designing a hybrid conductor solid-state air electrode with the core of carbon material as the electronic conductor and coating layer of solid electrolyte as the electronic conductor is promising in decreasing interfacial resistance and enhancing reaction kinetics of Na-O₂ batteries. Overall, developing an all-solid-state Na-O₂ battery is challenging, however it is vital for advancing the Na-O₂ technology.

In summary, considerable improvements have been made over the past few years regarding the superoxide-based Na-O₂ battery system, however the commercial and practical viability of this next-generation technology is still severely hindered. In order to realize high performance Na-O₂ batteries, an in-depth understanding of the cell electrochemistry and new strategies to fine tune the cell components to regulate NaO₂ formation are needed. Furthermore, the rational design of the air electrode structure and stabilization of metallic Na anode are key research areas that can accelerate the development of Na-O₂ cells and facilitate a sustainable world that runs on Na-O₂ batteries with high capacity and long cycle life.

CRediT authorship contribution statement

Xiaoting Lin: Investigation, Conceptualization, Writing – original draft, Writing – review & editing. **Qian Sun:** Conceptualization, Writing – review & editing. **Jung Tae Kim:** Writing – review & editing. **Xifei Li, Jiujun Zhang:** Writing – review & editing, **Xueliang Sun:** Writing – review & editing, Funding Support.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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