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Review

Sodium–Oxygen Batteries: Recent Developments and Remaining Challenges

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Sodium–oxygen (Na-O$_2$) batteries are considered a higher-energy-efficiency alternative to the lithium–oxygen (Li-O$_2$) system. The reversible superoxide electrochemistry governing the oxygen reduction and evolution reactions in Na-O$_2$ cells results in a relatively lower charging overpotential. Thus, significant research attention has been directed toward Na-O$_2$ in the hope of developing a high-energy-storage system. This review provides a brief overview of the most recent research progress in this field with special emphasis on the chemical and electrochemical reaction mechanisms. All major components of the cell including the positive and negative electrodes as well as the electrolyte are covered. Moreover, areas requiring more research attention are specified and potential directions for future research are proposed.

Na-O$_2$ versus Li-O$_2$ Batteries

Widespread application of fossil fuels by humankind during the few past decades has dramatically increased the greenhouse-gas concentration in the atmosphere, causing an unprecedented rise in the Earth's temperature. Thus, there is an urgent need to reduce the devastating consequences of global warming by decreasing the consumption of fossil fuels. Since the major portion of these fuels is consumed for transportation purposes, a switch from combustion engines to electric vehicles (EVs) has attracted a great deal of attention. Such EVs require a reliable electrical-energy-storage system that can compete with gasoline in terms of travel range and cost. Lithium-ion (Li-ion) batteries are currently employed as the state-of-the-art technology in this regard [1]. However, the available Li-ion technology cannot meet the current demands of electrical transportation. Therefore, the development of new battery systems with higher energy density and lower cost is required.

Alkali-metal–oxygen batteries (Li-O$_2$ and Na-O$_2$) provide the highest theoretical energy densities among all of the electrical-energy-storage systems, making them ideal systems for the current demand in portable energy storage [1,2]. However, several technical challenges must be addressed before these battery systems can be employed in practical applications. Relying on quasi-reversible oxygen/**peroxide** (see Glossary) (O$_2$/O$_2^{2-}$) electrochemistry, Li-O$_2$ cells particularly suffer from high charging **overpotential** that results in poor energy efficiency. In other words, more energy is required to recharge the battery compared with the energy that can be obtained on discharge. This high charging overpotential also contributes to instability of the cell components, leading to a low cycling performance [3]. Conversely, Na-O$_2$ cells exhibit lower charging overpotential, owing to the reversible oxygen/**superoxide** (O$_2$/O$_2^-$) electrochemistry. Thus, these cells are expected to display improved cycling performance and higher energy efficiency. Moreover, sodium is much more sustainable and cost-effective than lithium. Accordingly, the Na-O$_2$ battery system has attracted considerable research interest in the past few years [4].

Despite the lower charging overpotential, Na-O$_2$ cells do not exhibit a significant improvement over their Li counterparts in terms of cycling performance. Several side reactions at the cathode, anode, and electrolyte restrict the cycling life in Na-O$_2$ cells. This review intends to highlight the major findings and remaining challenges for Na-O$_2$ cells (Figure 1) and provide potential future research directions in this field.

General Working Principles

Na-O$_2$ cells pair metallic Na with O$_2$ as the negative and positive electrode materials, respectively, to produce a current flow. An aprotic electrolyte is thus required as the ion-conducting medium at the Na side due to the reactivity of metallic Na in **protic** solvents. On discharge, Na provides electrons

Highlights

The Na-O$_2$ battery has emerged as an energy-efficient and low-cost alternative to Li-O$_2$ batteries. Relying on reversible superoxide chemistry, Na-O$_2$ cells exhibit lower charging overpotential compared with their Li counterparts, which can be translated to high cycling performance.

Sodium superoxide (NaO$_2$) has been detected as the major discharge product of the cell in ether-based electrolytes, which can deliver a theoretical energy density of 1105 Wh kg^{-1}. The decomposition reaction of the obtained NaO$_2$ on charge requires a small overpotential (charging is generally performed below 3 V vs Na/Na$^+$), which reduces the risk of oxidative decomposition of the other cell components.

Both the positive and the negative electrode materials employed in the Na-O$_2$ system (i.e., Na and O$_2$) are among the most abundant elements on the Earth, making it one of the most sustainable, environmentally benign, and affordable battery systems.

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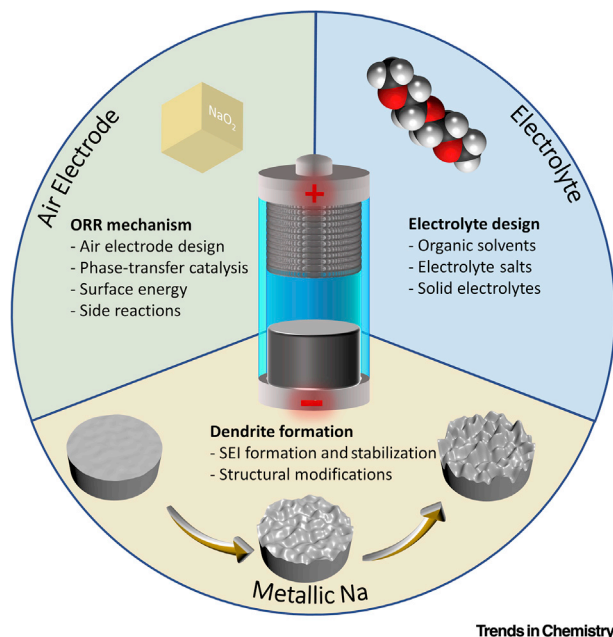
Trends in Chemistry

Figure 1. Major Challenges Facing the Development of Na-O₂ Batteries.

and Na⁺ ions, which migrate separately toward the positive electrode (also known as the air electrode). The transferred electrons reduce the molecular oxygen on the positive electrode and produce insoluble sodium oxide(s) in the presence of Na⁺ ions. The resulted discharge product is stored on the air electrode before it decomposes back to oxygen and metallic Na on charge [2].

The first report on a Na-O₂ cell was given by Peled and colleagues, who employed liquid sodium (at a temperature above the sodium melting point, 97.8°C) to address the dendrite formation seen in Li-O₂ cells [5]. A room-temperature Na-O₂ cell using a nonaqueous carbonate-based electrolyte was later investigated by Sun and colleagues, in which a mixture of sodium peroxide (Na_2O_2) and sodium carbonate was found as the discharge product [6]. Shortly after that, Hartmann and colleagues showed that sodium superoxide (NaO_2) is formed as the major discharge product using an ether-based electrolyte [7]. The obtained superoxide cell exhibited a small charging overpotential, owing to the following reversible electrochemical reaction:

$$Na \rightarrow Na^+ + e^- \qquad [1]$$

$$O_2 + e^- \rightarrow O_2^- \qquad [2]$$

The overall cell reaction is

$$Na + O_2 \leftrightarrow NaO_2 \qquad [3]$$

It has been shown that the oxygen reduction reaction (ORR) in both Li- and Na-O₂ cells involves the formation of superoxide (O_2^-) intermediates that then combine with Li⁺/Na⁺ in the cell electrolyte, forming dissolved $Li^+O_2^-$/$Na^+O_2^-$ ion pairs [8,9]. However, the relatively small Li⁺, a hard Lewis acid, cannot effectively stabilize the highly reactive O_2^-, a soft Lewis base, resulting in further oxidation (chemically or electrochemically) of O_2^- to O_2^{2-} and the formation of Li_2O_2 as the major product in Li-O₂ cells. Comparatively, the softer Na⁺ with higher polarizability can more efficiently stabilize O_2^-, and NaO_2 precipitates as the major discharge product of Na-O₂ cells. Decomposition of
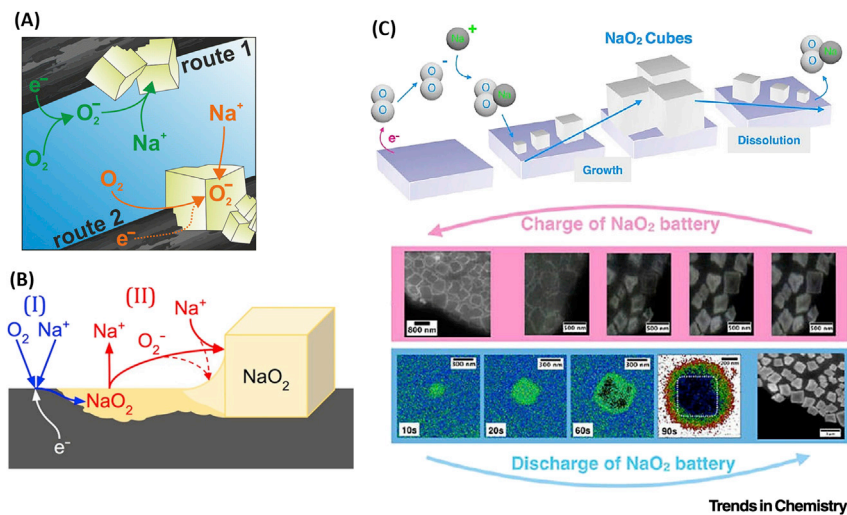
Figure 2. The Mechanism of the Oxygen Reduction Reaction in Na-O$_2$ Cells.
Different potential routes for growth of NaO$_2$ product (A), from [12] with permission. Schematic of the proposed mechanism for the discharge process based on a solution-mediated regime (B), from [13] with permission. Schematic of the electrochemically induced discharge and charge processes obtained based on *operando* transmission electron microscopy (TEM) observation (C), from [14] with permission.

superoxide-based products follows a single-electron-transfer pathway and hence requires a relatively small overpotential, whereas the decomposition reaction of peroxide-based products involves a more complicated two-electron transfer and requires a much higher overpotential on charge. Accordingly, superoxide cells generally exhibit lower charging overpotential and higher energy efficiency than their peroxide counterparts [10]. Nevertheless, several side reactions involving all components of the cell limit the cycling performance of superoxide cells.

Revealing the electrochemical reaction mechanisms in these cells using conventional analytical techniques is challenging because of the extremely sensitive nature of the intermediate species. *In situ* and *operando* spectroscopic techniques can provide real-time and accurate information about the system under the study. The application of *in situ* and *in operando* techniques combined with conventional analytical tools to comprehend the electrochemical reaction mechanism in Na-O$_2$ cells is discussed in the following section.

Electrochemical Reactions at the Air Electrode
ORR Reaction Mechanism: Solution Mediated versus Surface Mediated
The chemical composition of the discharge product in Na-O$_2$ cells is one of the main determining factors regarding energy efficiency as its main advantage over Li-O$_2$. Multiple oxides of various compositions have been detected in Na-O$_2$ cells as the discharge product [2,11]. Controlling the chemical composition of the products is essential to maintain the low charging overpotential by conducting the discharge reaction toward the formation of oxygen-rich products. A good summary of the experimental control parameters can be found in [11]. As previously mentioned, ORR in aprotic solvents involves the formation of O$_2^-$ intermediates in the first step. In the presence of soft Na$^+$, NaO$_2$ forms and precipitates as large cubic crystalline products [7]. Using *ab initio* calculations, Hartmann and colleagues estimated the bandgap of stoichiometric NaO$_2$ to be about 2.0 eV, which makes it electrically insulating [12]. Meanwhile, the authors estimated the solubility of NaO$_2$ in diglyme-based electrolyte using a dual-working electrode setup as 10^{-4} g mol^{-1} and concluded that a solution-mediated mechanism is responsible for the growth of micrometer-sized NaO$_2$ cubes (route 1 in Figure 2A). A similar mechanism was later shown for low current densities by Nichols and colleagues (Figure 2B) [13].

The solution-mediated mechanism was further confirmed by *operando* **electron spin resonance (ESR)** spectroscopy results, where dissolved O_2^- species were stabilized by a cold spin-trapping technique and detected using the ESR signal [9]. In addition, more direct microscopic evidence toward the solution-mediated mechanism was recently obtained using *operando* transmission electron microscopy (TEM) in a liquid electrochemical cell (Figure 2C) [14]. One may also consider the further oxidation of superoxide to form peroxide, similar to the ORR mechanism in Li-O_2 cells [8,15]. The close thermodynamic stabilities of NaO_2 ($\Delta G° = -437.5$ kJ mol^{-1}) and Na_2O_2 ($\Delta G° = -449.7$ kJ mol^{-1}) implies that both species are likely to form as the ORR products [16,17]. However, the formation of NaO_2 through a single-electron-transfer reaction is more kinetically favorable than a two-electron transfer in the case of Na_2O_2 [18]. In addition, larger Na^+ ions can more effectively stabilize O_2^- compared with Li^+ ions and hence prevent the disproportionation reaction of formed NaO_2 to Na_2O_2. As a result, NaO_2 is the primary discharge product of Na-O_2 cells in relatively stable aprotic electrolytes. A number of factors, however, contribute to altering the chemical composition of the discharge products in Na-O_2 cells, which are covered in the following sections.

Phase Transfer Catalysis: The Role of Protic Additives

Na-O_2 cells are extremely sensitive to the presence of humidity in the cell environment. Xia and colleagues demonstrated that the presence of water (as well as other protic solvents; e.g., acetic and benzoic acids) at the ppm level may promote the formation of NaO_2 by changing the growth mechanism from surface mediated to solution mediated [19]. Protic additives increase the solubility of O_2^- in the cell electrolyte by providing free protons to form soluble HO_2 intermediates, which then react with Na^+ and precipitate as NaO_2. Moreover, following studies indicated that the addition of up to 6000 ppm of water did not initiate the formation of side-products in Na-O_2 cells [20,21]. A similar effect of water on the growth mechanism of products has been also observed in Li-O_2 cells [22].

Water plays an ambivalent role in Li/Na-O_2 cells by increasing the capacity via conducting the reaction mechanism through a solution-mediated regime on the one hand and enhancing singlet oxygen ($^1O_2$) formation on the other hand. $^1O_2$ is the first excited state of triplet ground-state dioxygen and may be formed by chemical oxidation of alkaline peroxides in nonaqueous media. Using an *operando* fluorescence probe, Freunberger and colleagues showed that $^1O_2$ is produced during both discharge and charge of Li/Na-O_2 cells [23,24]. It was also found that the $^1O_2$ content substantially increases during the charging as the potential rises or with the addition of trace water to the electrolyte [24]. They demonstrated that the formation of $^1O_2$ in typical ether-based electrolytes leads to the same decomposition products (carbonate, acetate, and formate) as previously reported in Li-O_2 cells.

Exposure of the discharge products to moisture may effectively transform the composition of the products. A study on the effect of the relative humidity (RH) level in the gas phase on the performance of Na-O_2 cells revealed that both the discharge capacity and the cell voltage increased with increasing RH [25]. In addition, sodium hydroxide (NaOH), a hydrated form of peroxide ($Na_2O_2.2H_2O$), and sodium carbonate (Na_2CO_3) were found as side-products under high RH. Meanwhile, it was shown using an *operando* X-ray diffraction technique that the presence of moisture in the gas phase feeding the cell may result in the formation of $Na_2O_2.2H_2O$ according to the following reaction (Figure 3A) [26]:

$$2Na^+ + O_2 + 2H_2O + 2e^- \leftrightarrow Na_2O_2.2H_2O \qquad [4]$$
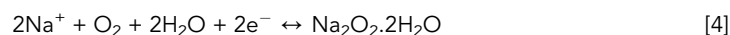
Moreover, the role of moisture in the gas phase on the composition of discharge products was further confirmed by examining different cell configurations. Zhao and colleagues found NaO_2 as the major product of the cell using a static Ar/O_2 (80/20 vol%) atmosphere, whereas $Na_2O_2.2H_2O$ was obtained under flowing pure oxygen [27]. Furthermore, Bi and colleagues showed that while NaO_2 forms as the major product in the air-tight stainless-steel cell, $Na_2O_2.2H_2O$ was the major product in the glass-chamber cell-configuration (Figure 3B) [28]. These studies highlight the extreme sensitivity of Na-O_2 cells to environmental parameters and experimental conditions. It should be emphasized that the oxygen gas fed into the cell should be completely dry to acquire pure NaO_2.
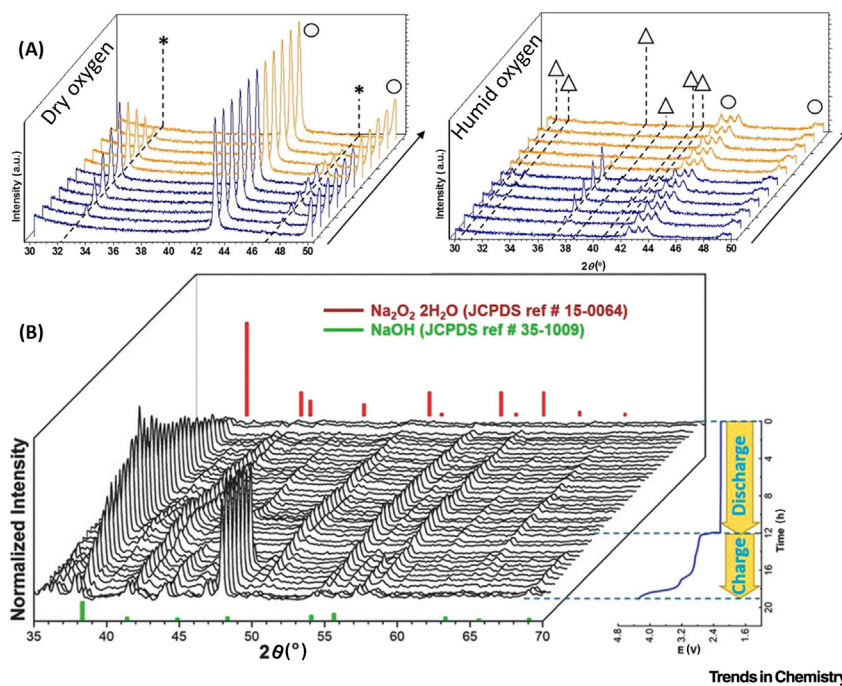
Figure 3. Effect of Moisture in the Gas Phase Feeding into Na-O$_2$ Cells.
Operando X-ray diffraction patterns recorded for cells discharged and charged under dry and humid conditions (A), from [26] with permission. *Operando* X-ray diffraction (XRD) of Na-O$_2$ cell tested in a glass-chamber cell (B), from [28] with permission.

Role of Surface Energy of the Air Electrode on Composition and Morphology of Products

The air electrode may also alter the ORR reaction mechanism, although it is not electroactive itself. Different types of carbon electrodes were examined as the air electrode of Na-O$_2$ cells by Bender and colleagues, where NaO$_2$ was found to be the main product in all cases [16]. However, a wide range of **specific capacities** from 300 to 4000 mAh g^{-1} were obtained depending on the type of air electrode. In addition, microscopic inspection of the discharged electrodes displayed typical NaO$_2$ cubes on some electrodes, while amorphous products were found on others. The influence of the air electrode surface on the morphology of the products was later studied by comparing the electrochemical behavior of carbon and gold surfaces [29]. Both electrodes demonstrated comparable redox processes toward the formation and decomposition of NaO$_2$ using cyclic voltammetry measurements. However, in contrast to the carbon surface, the Au air electrode exhibited a four-times-smaller discharge capacity and flake-like discharge products. According to the authors, the higher surface energy and larger O$_2$/O$_2^-$ affinity of the Au surface facilitated the nucleation of products and altered the NaO$_2$ growth mechanism.

Yadegari and colleagues also illustrated the significant effect of oxygen-containing functional groups at the surface of carbonaceous electrodes on both the morphology and the composition of products in Na-O$_2$ cells [30]. The oxygen-containing functional groups on a hydrophilic surface catalyzed the ORR and conducted the reaction mechanism toward the peroxide pathway by adsorbing the O$_2^-$ intermediate at the electrode surface, whereas the lowered interaction of hydrophobic surfaces with the reaction intermediates facilitated a solution-mediated mechanism, which resulted in formation of large cubic NaO$_2$. These results highlight the importance of the electrode surface properties in designing efficient air electrodes for Na-O$_2$ batteries.
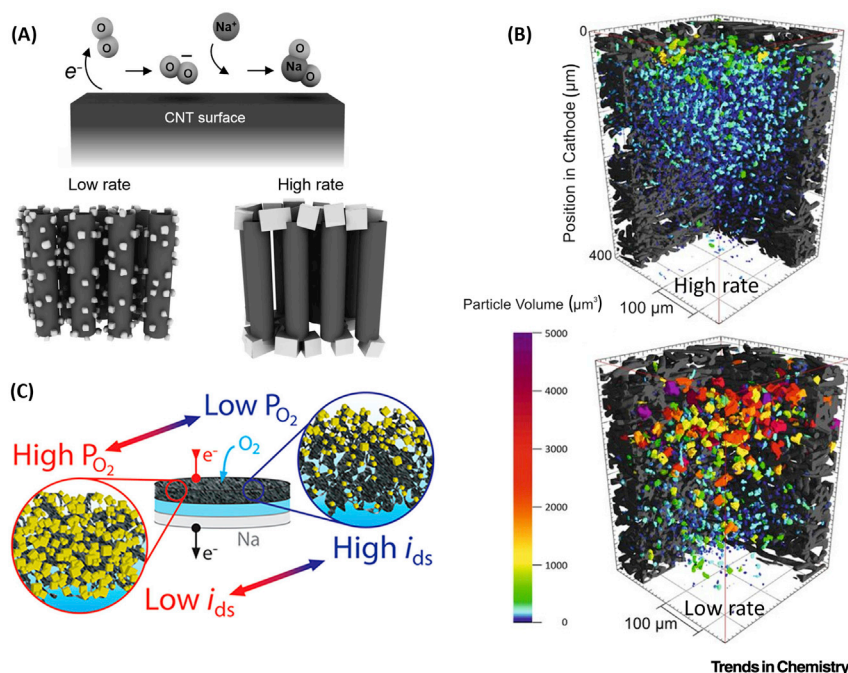
Figure 4. Formation of Discharge Products and the Air Electrode Design.
Distribution of products on the air electrode discharged under different low and high rates (A), from [20] with permission. Particle size distribution analysis inside the air electrode (B), from [32] with permission. The influence of oxygen pressure on the formation of discharge products (C), from [34] with permission.

Effect of Air Electrode Design on Cell Performance

Carbon has been the material of choice for air electrode applications mainly because of its good electrochemical stability and electrical conductivity, low cost, and ease of preparation in various forms and shapes. Multiple forms of carbonaceous air electrodes have been developed and examined in Na-O_2 cells [2]. A systematic study on the influence of the porosity and surface area of the air electrode revealed that the discharge capacity of Na-O_2 cell has a direct correlation with the surface area in the mesoporous region [31]. Meanwhile, inspection of the air electrode discharged in Na-O_2 cells under different low and high rates showed distinct features for the formation of products [20,32,33]. While larger crystalline products were formed at the superficial sites of the air electrode under higher discharge rates, the products displayed more uniform distributions in size and growth locations under lower discharge rates (Figure 4A,B). This phenomenon was explained based on the relatively fast nucleation of NaO_2. In addition, oxygen pressure has been shown to influence the discharge–charge mechanisms (Figure 4C) [34]. These studies indicate that kinetics play a more significant role in the morphology of the discharge products in Na-O_2 cells compared with their Li counterparts.

To address the mass-transfer limitations in the air electrode, Yadegari and colleagues designed a 3D air electrode with a dual-porous system comprising vertically aligned nitrogen-doped carbon nanotubes on carbon paper [35]. Despite a significant improvement in discharge capacity, X-ray absorption analysis of the air electrode after cycling showed that carbon is not chemically stable against the highly oxidative reaction intermediates and discharge products. The instability of carbon in the Li-O_2 cell environment has also been proved by a number of studies [36,37]. An alternative design for the air electrodes in alkali-metal–O_2 cells involves the synthesis of a 3D lightweight carbonaceous framework with a protective layer, which can prevent the oxidation of the electrode surface and act as an electrocatalyst [38,39]. Future research on air electrode design and fabrication should be focused on carbon-free porous materials with high chemical stability in the oxidative environment of the cell.

Electrolyte Design for Na-O$_2$ Cells

The instability of the electrolyte solvents in Na-O$_2$ cells also contributes to alter the chemical composition of the products. As previously mentioned, early attempts with Na-O$_2$ cells using carbonate-based electrolytes resulted in the formation of a mixture of Na$_2$O$_2$ and Na$_2$CO$_3$ [6]. The formation of carbonate-based side-products is an outcome of the O$_2^-$ nucleophilic attack against the ethereal C atoms of the CH$_2$ groups in carbonate-based solvents [40]. Similar decomposition reactions have been observed in Li-O$_2$ cells too [41]. An overview of the influence of cell electrolyte on the performance of Na-O$_2$ cells is provided here.

Organic Solvents

Following the shift from carbonate to ether-based electrolytes in both Li- and Na-O$_2$ cells, McCloskey and colleagues demonstrated by **differential electrochemical mass spectrometry (DEMS)** that fewer decomposition reactions involving the electrolyte/air electrode occur in Na-O$_2$ cells compared with their Li counterparts during the first discharge–charge cycle [10]. Subsequently, Zhao and colleagues reported a correlation between the NaO$_2$ content of the cell product and the pK_a of the corresponding solvent, suggesting that application of solvents with larger pK_a would be beneficial toward the formation of NaO$_2$ [42]. Afterward, a study by Lutz and colleagues demonstrated that the utilization of ethers with shorter alkyl chains as the electrolyte solvent results in significantly increased discharge capacities in Na-O$_2$ cells [43]. The authors explained the improved performance based on the moderate solvent–solute interactions, which facilitate the formation of contact-ion pairs and conducts the growth mechanism to a solution-mediated regime.

The Lewis basicity of the solvent may also influence the discharge products by conducting the growth mechanism toward either a solution- or a surface-mediated regime. An *in situ* surface-enhanced Raman spectroscopy (SERS) study on an Au surface indicated that the application of solvents with a lower **donor number (DN)** results in the formation of Na$_2$O$_2$ due to the inability of the solvent to form an ion pair [44], whereas solvents with higher DN contribute to dissolve the initially formed O$_2^-$ by pairing it with Na$^+$ and removing it from the electrode surface. The higher solubility of O$_2^-$ in the cell electrolyte may have other drawbacks as well.

Black and colleagues revealed that even ether-based electrolytes are not totally stable against nucleophilic attack by the dissolved O$_2^-$ [45]. The authors demonstrated that diglyme undergoes a decomposition reaction, mainly on discharge, producing sodium carboxylates (carbonate, formate, and acetate). It was also found that the amount of side-products significantly increases on exposure of the products to the cell electrolyte for 100 h. Similar results were obtained by a number of studies, confirming the increased formation of side-products as a result of resting the discharge product in contact with the ether-based electrolytes [46–51]. By contrast, using an operando TEM technique Kwak and colleagues showed that NaO$_2$ is relatively stable in the presence of solid electrolytes (SEs) (Figure 5A,B) [52]. More recently, Yadegari and colleagues developed an *in situ* Raman imaging technique to illustrate the mechanism of the decomposition reaction in Na-O$_2$ cells [53]. Our results revealed that oxalate-based side-products may form on the NaO$_2$ surface by exposure of the product to the cell electrolyte over a prolonged time (Figure 5C). Future studies should aim to fully unveil the reaction mechanisms at the product/electrolyte interface using advanced *operando* spectroscopic techniques.

Electrolyte Salts

The type and concentration of the electrolyte salt are shown to affect the performance of Na-O$_2$ cells. Lutz and colleagues reported that the type of anion in DME solvent does not have a notable influence on the formation of NaO$_2$ [54]. However, it may affect **solid electrolyte interface (SEI)** formation on the metallic sodium, where PF$_6^-$ can lead to the formation of a stable and conductive SEI and TFSI$^-$ can impose increased impedance into the cell over time. By contrast, Liu and colleagues reported that the application of OTF$^-$ anion in diglyme solvent as a weak solvation ether results in an improved discharge capacity, while PF$_6^-$ provides a lower capacity [55]. The DN of the anion is argued to play a role here, with higher-DN anions leading to increased discharge capacity.
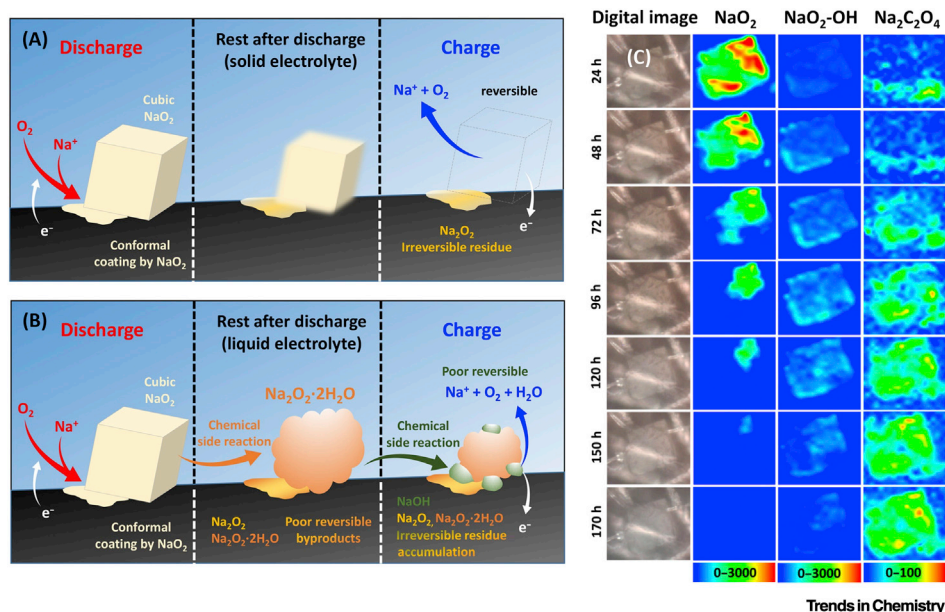
Figure 5. The Influence of the Cell Electrolyte on the Oxygen Reduction Reaction (ORR) Mechanism and Stability of Discharge Products.
Schematic diagram for the reaction mechanism of Na-O$_2$ cells without (A) and with (B) the proton source, from [52] with permission. The change of NaO$_2$ cube in contact with the cell electrolyte over time obtained by Raman imaging (C), from [53] with permission.

Meanwhile, a study by He and colleagues suggests that the concentration of electrolyte salt may affect the stability of the metallic Na in NaTFSI/DMSO electrolyte [56]. Using Raman spectroscopy, the authors showed that lower free DMSO molecules are available in the electrolyte with a higher concentration of NaTFSI. Thus, higher stability of metallic Na in concentrated electrolytes has been correlated with a reduction of free DMSO molecules. A similar approach was applied to investigate the effect of concentrated electrolyte (NaClO$_4$ in diglyme) on the stability of NaO$_2$ on resting in the cell [57]. The results suggested a reduced rate of decomposition reaction in concentrated electrolytes. However, the formation of side-products was not totally halted. Reduction of the free solvent molecules has been emphasized to play a role in reducing the rate of decomposition.

Nonetheless, the electrolyte viscosity significantly increases with an increase in the salt concentration, resulting in lower ionic conductivity and oxygen solubility, which compromises the discharge capacity [58,59]. Moreover, reduced amounts of free electrolyte may also lead to decreased solubility of the reaction intermediates, which in turn conduct the growth mechanism toward a surface-mediated regime. However, the opposite conclusion was made using a pyrrolidinium-based ionic liquid as the electrolyte solvent. Zhang and colleagues reported that higher concentrations of electrolyte salt resulted in a higher discharge capacity and improved cycling life [60]. The enhanced performance has been related to the increased interaction of O$_2^-$ with Na$^+$ instead of with ionic liquid cations. Further progress of Na-O$_2$ batteries critically relies on the development of efficient and stable electrolyte systems, which should be the focus of further investigations.

Solid electrolytes (SEs)

Application of SEs, including ceramic ion conductors and solid polymer electrolytes (SPEs), can eliminate the side reactions associated with the oxidative decomposition of organic solvents and protect the metallic Na electrode. An *operando* TEM study on a solid-state Na-O$_2$ cell using CuO nanowires as the air electrode revealed no carbonate formation during the battery cycling in the absence of

organic solvents and carbonaceous electrodes [61]. The same conclusion was derived from a similar study using a carbonaceous air electrode, confirming the role of organic electrolytes in formation of side-products in Na-O$_2$ cells [52]. The SE candidates should be stable against the extremely oxidative ORR intermediates and highly reducing metallic Na at the same time. Meanwhile, considering the solution-mediated mechanism in the formation of discharge products, developing a solid-state Na-O$_2$ cell with a discharge capacity comparable with liquid cells is a significant challenge. Accordingly, research on solid-state Na-O$_2$ cells is in its infancy [62]. Among ceramic SEs, Na-β''-Al$_2$O$_3$ and **NASICON** structures exhibit acceptable ionic conductivity while being stable against Na and O$_2$. The application of a NASICON ceramic as a separating barrier in a mixed aqueous/aprotic Na-O$_2$ cell demonstrated an energy density of 1500 Wh kg^{-1} and a discharge capacity of 600 mAh g^{-1} [63]. SPEs are more mechanically flexible, providing efficient solid–solid interfaces. However, SPEs exhibit low ionic conductivity at room temperature and research is ongoing to increase the ionic conductivity by introducing ceramic fillers into the SPEs structure [64].

Metallic Na Electrode

Na metal is more chemically reactive than Li and consequently its application in metal–O$_2$ cells involves additional side reactions as well as serious dendrite formation [2,27,65–68]. Dissolution of metallic Na on discharge results in cracking of the SEI layer and the formation of dendrite structures by deposition and growth of Na at the cracked sites on charge. The same phenomenon is responsible for the electrolyte consumption in the formation of a new SEI layer on the exposed and/or freshly deposited Na. A study by Bender and colleagues showed that the cycling performance of Na-O$_2$ cells may be improved by using sodiated carbon as the negative electrode [69]. Moreover, a recent study in our research group demonstrated that passivation of the metallic Na electrode as a result of oxygen and O$_2^-$ crossover from the air electrode may restrict the discharge capacity of the cell [70]. Therefore, various strategies, such as enveloping the metallic Na electrode by protective thin films as well as the application of 3D hosts and current collectors, have been adapted to improve the performance of the negative electrode as summarized in Figure 6. Recent progress in understanding the reaction mechanisms and application of metallic Na in various battery systems is summarized in [66].

SEI Formation and Stabilization

Protection of metallic Na electrodes can be generally achieved by: (i) modification of the cell electrolyte for *in situ* stabilization of the SEI through the adoption of additives; or (ii) the formation of an artificial SEI layer to prevent direct contact between the metallic Na and the cell electrolyte while maintaining Na$^+$ ion conduction. NaPF$_6$ electrolyte salt has been found to be beneficial toward the formation of a stable SEI layer in ether-based electrolytes [71]. Meanwhile, electrolyte additives such as Na$_2$S$_6$ and K$^+$ ions (Figure 6A) are reported to enhance the cycling performance of metallic Na in ether-based electrolytes [72,73]. In addition, concentrated electrolytes are argued to promote the stability of metallic Na by decreasing the uncoordinated solvent molecule and interfacial impedance [74]. Nonetheless, the increased concentration also results in high viscosity, poor wettability, and reduced oxygen dissolution, which compromises the discharge capacity. Various strategies for SEI engineering are summarized in a recent review by Matios and colleagues [64].

The formation of a Na$^+$-permeable yet flexible protective layer (an artificial SEI) is another approach to prevent dendrite growth in metallic Na cells. The application of a few layers of free-standing graphene (2.3 nm) on metallic Na is shown to effectively improve the cycling performance [75]. Through direct reaction between 1-bromopropane and the Na surface, Choudhury and colleagues prepared a homogeneous, 2—10-μm-thick NaBr coating, which exhibited stable cycling performance for 250 cycles at 0.5 mAh cm^{-2} (Figure 6B1) [76]. Gas-phase reactions such as atomic and molecular layer deposition (ALD and MLD) enable the deposition of uniform and controllable organic and inorganic films. Accordingly, the application of atomically deposited films such as Al$_2$O$_3$ and alucone (Al-ethylene glycol) to form an artificial SEI layer has been extensively reported (Figure 6B2) [77–79].

SEI Formation and Stabilization

Electrolyte additives

Artificial SEI layer

Structural Modifications

Nanostructured current collectors
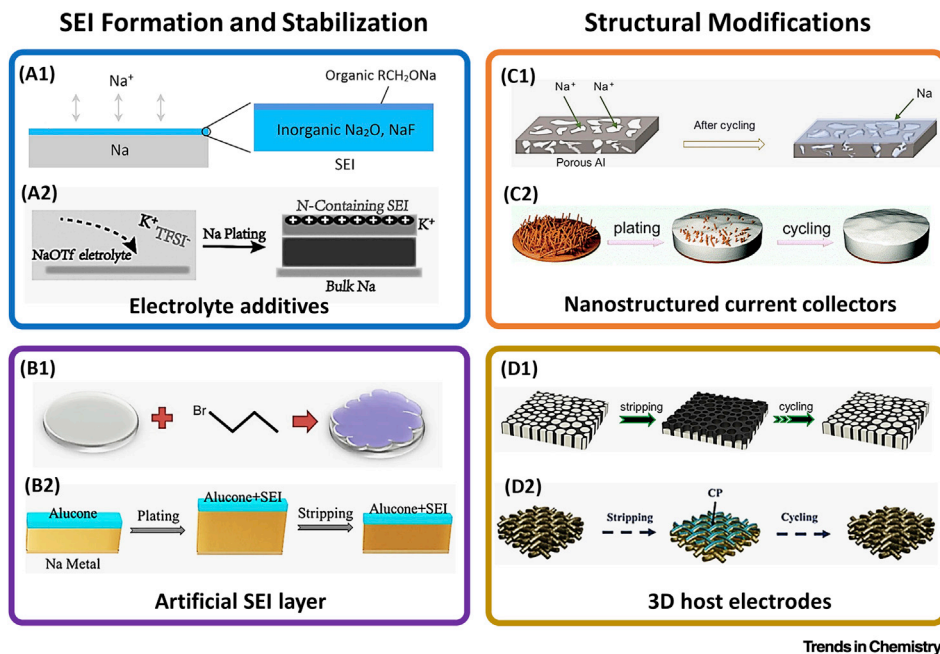
3D host electrodes

Figure 6. Various Strategies Adopted to Improve the Cyclic Performance of Metallic Na Electrode.
Modification of cell electrolyte for *in situ* stabilization of solid electrolyte interface (SEI) by addition of Na_2S_6 (A1), from [71] with permission, and K^+ ion (A2), from [72] with permission. Formation of artificial SEI layers using direct reaction at the Na surface (B1), from [76] with permission, or molecular layer deposition (B2), from [77] with permission. Application of porous Al foil (C1), from [80] with permission, and 3D Cu nanowires (C2), from [81] with permission, as nanostructure current collectors. Application of wood-derived carbon (D1), from [82] with permission, and N-doped carbon nanotubes on carbon paper (D2), from [84] with permission, as 3D host electrodes.

Structural Modifications

Structural modification of the metallic Na electrode concerns the spatial inhomogeneity of the Na^+ distribution on the electrode surface as a potential reason for dendrite growth. To address the Na^+ inhomogeneity, researchers have tried to increase the active surface area of the negative electrode by creating nanostructured electrodes as either current collectors or hosts for metallic Na. For instance, the application of porous Al foil and 3D Cu nanowires (Figure 6C1,2) as current collectors is shown to suppress dendrite growth in metallic Na cells [80,81]. Alternatively, the application of light, nanostructured carbonaceous host electrodes such as reduced graphene oxide (rGO) aerogel, wood-derived carbon with porous channels (Figure 6D1), or N-doped carbon nanotubes on carbon paper (Figure 6D2) reduces the inactive mass in the electrode structure while demonstrating stable cycling performance [82–84]. Moreover, these nanostructured electrodes enable stable cycling performance of the cell at high current densities, which is not achievable with conventional metallic Na. Despite a number of recent reports on improving the cycling performance of metallic Na electrodes, more studies are required to understand the mechanism of passivation reactions in Na-O_2 cells and to develop practical solutions to improve its performance in the harsh environment of the cell. Special attention should be given to protect the metallic Na from oxygen, superoxide, and singlet oxygen species, which migrate from the positive to the negative electrode. Similar strategies employed in Li/Na-S cells to stop polysulfide migration including modification of the air electrode and the application of porous interlayers can be adapted for Na-O_2 cells.

Concluding Remarks

Na-O_2 batteries have raised hopes for the development of a high-energy-storage technology at low cost. This system exhibits a lower charging overpotential and higher energy efficiency than the Li-O_2

Outstanding Questions

Instability of organic electrolytes is still one of the biggest challenges facing the development of Na-O_2 battery systems. Although finding a desirable electrolyte for the Na-O_2 system is less challenging than for Li-O_2 due to the narrower required electrochemical window, the search for a stable electrolyte system is ongoing.

A desirable electrolyte for the Na-O_2 system should exhibit high chemical stability against the superoxide (O_2^-) reaction intermediate, a wide electrochemical window, high oxygen solubility, low vapor pressure, and adequate ionic conductivity. Is it possible to collect all of these requirements in a single solvent?

Solid-state electrolytes present desirable characteristic in terms of chemical and electrochemical stability compared with organic electrolytes. How can we adapt solid-state electrolytes to the air electrode in Na-O_2 cells, where the discharge product is produced through a solution-mediated mechanism?

The dissolved oxygen and O_2^- intermediate may cross over from the air electrode and passivate the Na surface. How can we provide practical protective strategies to prevent oxidation of the Na surface as well as suppress dendrite formation?

It has been shown that a solution-mediated growth mechanism at the air electrode improves the discharge capacity of the cell by enhancing the migration of O_2^- intermediates away from reaction sites. How can we prevent the dissolved intermediates from precipitating on the separator or reaching the negative electrode and being involved in nonelectrochemical reactions?

How can we improve the air electrode design to reduce the migration of the reaction intermediates away from the air electrode while maintaining large discharge capacities?

battery system, owing to the reversible superoxide electrochemistry governing the ORR/OER mechanism at the air electrode. The superoxide electrochemistry results from the stabilizing effect of the relatively softer Na^+ ion in neutralization of the highly oxidative O_2^- intermediate species. However, the interaction between the ion pair is not enough to prevent the nucleophilic attack of O_2^- against the cell electrolyte. Even the precipitated NaO_2 gradually reacts with the electrolyte, resulting in reduced Coulombic efficiency due to the passivation of the electrode surface. In addition, the intrinsic stability of NaO_2 is a matter of debate. Instability of the available organic solvents is one of the major obstacles that restrict the further development of Na-O_2 batteries (see Outstanding Questions). More *in situ* studies are required to fully understand the degradation mechanisms at the electrode/electrolyte interface. In addition, the application of mixed electrolyte systems to reduce the free organic solvents or electrolyte additives with stabilizing effect toward O_2^- intermediates could be considered as a potential solution in this regard.

The higher chemical reactivity of metallic Na is another significant challenge facing the progress of Na-O_2 batteries. The dissolved oxygen in the cell electrolyte as well as the superoxide intermediates formed at the air electrode may migrate toward the negative electrode under a concentration gradient and/or electric-field forces. The crossed-over species passivate the metallic Na and restrict the discharge capacity by imposing an additional overpotential on the cell. Moreover, the consumed reaction intermediates in this process decrease the Coulombic efficiency of the cell. Accordingly, future research should endeavor to minimize oxygen and superoxide migration by improving the air electrode design. Meanwhile, electrolyte solvents with higher stability against oxidative decomposition should be developed. Blending organic solvents or ionic liquids to achieve a desirable electrolyte with optimized properties and improved stability can be considered as a potential research path. In addition, the application of SEs may prevent oxygen and superoxide cross over toward metallic Na, suppress dendrite formation at the negative electrode, and address the instability problem related to the organic electrolytes. A combination of SEs and liquid electrolytes can protect the metallic Na electrode and suppress dendrite formation while maintaining a high discharge capacity through a solution-mediated ORR mechanism.

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