ACCOUNTS of chemical research

Article

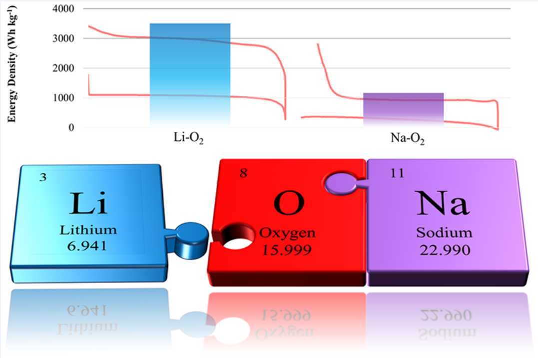
Cite This: *Acc. Chem. Res.* XXXX, XXX, XXX−XXX

pubs.acs.org/accounts

Recent Advances on Sodium−Oxygen Batteries: A Chemical Perspective

Hossein Yadegari and Xueliang Sun*

Department of Mechanical & Materials Engineering, University of Western Ontario, London, Ontario N6A 5B9, Canada



CONSPECTUS: Releasing greenhouse gases into the atmosphere because of widespread use of fossil fuels by humankind has resulted in raising the earth's temperature during the past few decades. Known as global warming, increasing the earth's temperature may in turn endanger civilization on the earth by starting a cycle of environmental changes including climate change and sea level rise. Therefore, replacing fossil fuels with more sustainable energy resources has been considered as one of the main strategies to tackle the global warming crisis. In this regard, energy saving devices are required to store the energy from sustainable resources like wind and solar when they are available and deliver them on demand. Moreover, developing plug-in electric vehicles (PEVs) as an alternative for internal combustion engines has been extensively pursued, since a major sector of fossil fuels is used for transportation purposes. However, currently available battery systems fail to meet the required demands for energy storage.

Alkali metal−O_2 battery systems demonstrate a promising prospect as a high-energy density solution regarding the increasing demand of mankind for energy storage. Combining a metallic negative electrode with a breathing oxygen electrode, a metal−O_2 cell can be considered as a half battery/half fuel cell system. The negative electrode in the metal−O_2 cells operates a conversion reaction rather than intercalation mechanism, which eliminates the need for a host lattice. In addition, the positive electrode material (O_2) comes from the ambient air and hence is not stored in the battery. Therefore, the resultant battery systems exhibit the highest theoretical energy density, which is comparable to that of gasoline. Accordingly, an unprecedented amount of research activity was directed toward alkali metal−O_2 batteries in the past decade in response to the need for high-energy storage technology in electric transportation. This extensive research surge has resulted in a rapid expansion of our knowledge about alkali metal−O_2 batteries. The present Account summarizes the most recent findings over the underlying chemistry of all components in Na−O_2 cells as one of the most efficient members of alkali metal−O_2 family.

1. INTRODUCTION

Alkali metal−oxygen (Li/Na−O_2) batteries have received a great deal of research attention during the past couple of decades as the next generation of electrical energy storage systems.[1,2] Li/Na−O_2 batteries provide the highest energy densities among all the available systems by coupling a high energy metallic Li/Na negative electrode with a breathing O_2 electrode, which is also referred as an air electrode. An aprotic electrolyte compatible with metallic Li/Na negative electrode is hence required to conduct the positive ions (Li^+/Na^+) within the cell. The metallic ions produced during the discharge cycle combine with the reduced oxygen on the air electrode surface to form the solid discharge products. The resultant discharge products are thus required to be stored at the air electrode before decomposing back to gaseous oxygen and metallic ions on charge.

Although the oxygen reduction and evolution reactions (ORR and OER) in aqueous electrolytes have been relatively well-studied, our knowledge about the reaction mechanism in nonaqueous electrolytes is limited to the studies in the past several years. Aside from the immature perception of the working principles of the cells, there are also multiple challenges associated with all components of Li/Na−O_2 batteries. Foremost among them is the large overpotential required for decomposition of the solid discharge products in the charge cycle of peroxide cells, which decreases the energy efficiency of the battery system. Multiple factors contribute to the large charging overpotential in these cells including the irreversible nature of the electrochemical reaction, poor electric conductivity of the discharge products, and formation of insulating parasitic side-products on the air electrode. In addition, imposing a large positive potential toward the air electrode during the charge cycle results in instability of the electrode materials (mainly carbonaceous) and decomposition of the cell electrolyte. Overcoming the large charging overpotential is one of the major challenges, particularly facing the development of Li−O_2 batteries.

Meanwhile, relatively lower charging overpotential has directed more research attention toward Na−O_2 cells, despite their lower theoretical energy density (1105 Wh kg^{-1}) compared with that of Li−O_2 (3505 Wh kg^{-1}). The lower charging overpotential seen in Na−O_2 cells is mainly due to the reversible electrochemistry of oxygen/superoxide (O_2/O_2^-)

Received: March 27, 2018

DOI: 10.1021/acs.accounts.8b00139
Acc. Chem. Res. XXXX, XXX, XXX−XXX

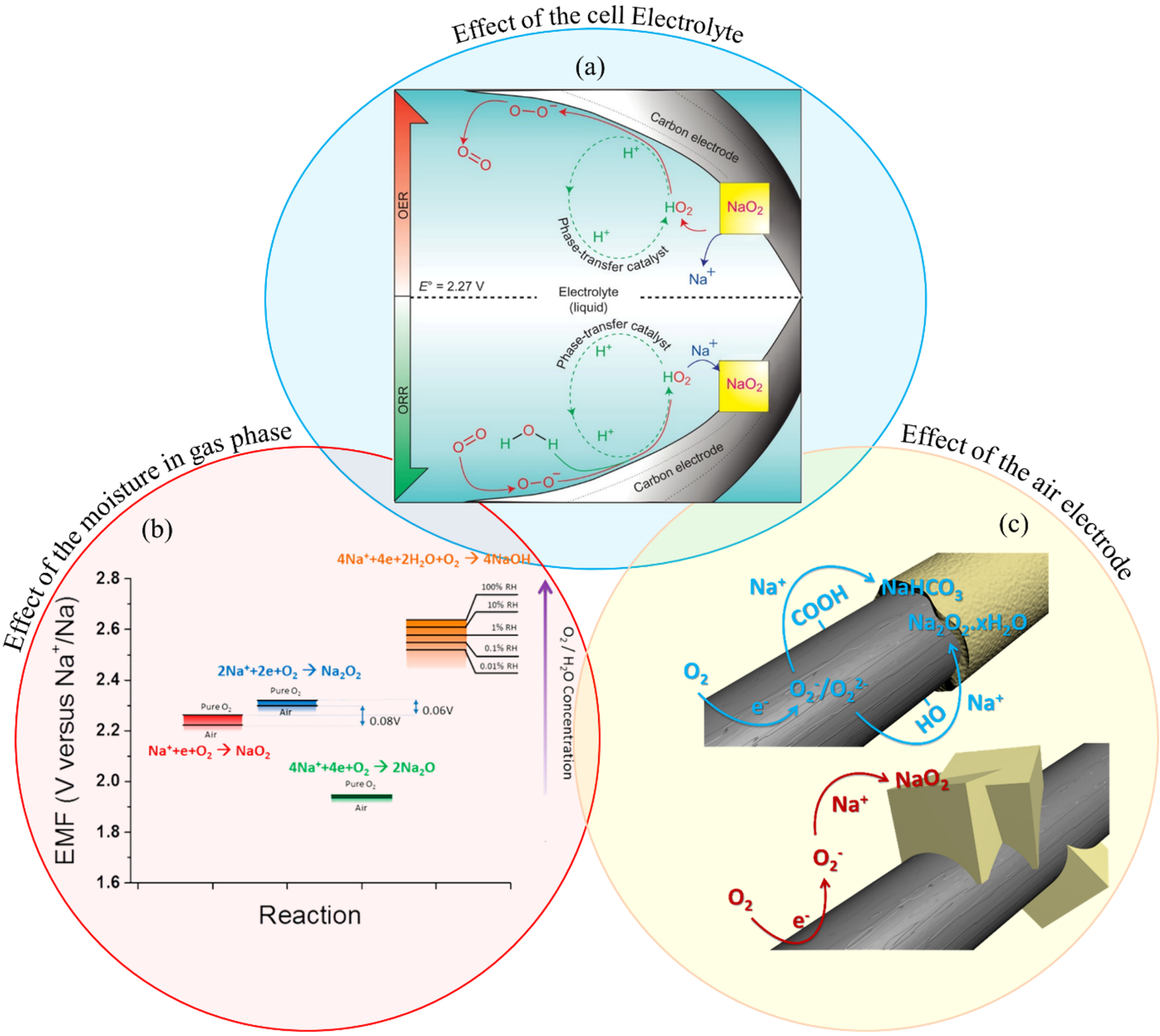


Figure 1. Schematic diagram for the effect of various components on the composition and morphology of the products in Na−O_2 cells including the effect of proton transfer catalysis (a) (Reproduced with permission from ref 6. Copyright 2015 Nature Publishing Group), effect of the moisture in the gaseous phase (b) (Reproduced from ref 12. Copyright 2015 American Chemical Society), and the role of oxygen-containing functional groups (c) (Reproduced from ref 15. Copyright 2017 American Chemical Society).

redox pair, compared to the semi-irreversible oxygen/peroxide (O_2/O_2^{2-}) pair in Li−O_2 cells.[3] Nevertheless, a precise control over the electrochemical pathway in Na−O_2 cells is essential in order to maintain the low charging overpotential. Furthermore, metallic Na plays a more determining role in the overall performance of Na−O_2 cells compared to its Li counterpart. Therefore, understanding the working principles of metallic Na electrode and aprotic cell electrolyte in contact with O_2 and O_2^- intermediates existing in the harsh environment of Na−O_2 cells is required.

In this Account, attention will be given to the electrochemical reaction mechanisms involving the main components of Na−O_2 cells including the positive air electrode, negative Na electrode, and cell electrolyte. The significant findings toward the reaction mechanism of the cell components will be summarized, and the key similarities and differences with Li−O_2 cells will be provided. The potential future research directions will also be discussed.

2. SUPEROXIDE VERSUS PEROXIDE CHEMISTRY

Charging overpotential in Li/Na−O_2 cells is directly correlated to the chemical composition of the discharge products. Meanwhile, the ORR mechanism at the air electrode mainly determines the composition of the products. ORR in aprotic solvents has been proven to involve the formation of O_2^- intermediates.[1] The O_2^- intermediates combine with Li^+ ions in Li−O_2 cells, forming thermodynamically unstable LiO_2, which eventually transforms (chemically or electrochemically) to the more stable Li_2O_2. Li−O_2 cells with Li_2O_2 as the dominant discharge product exhibit a relatively large charging overpotential (>1 V), mainly due to the semi-irreversible O_2/O_2^{2-} electrochemistry. In the case of Na−O_2 cells, however, Na^+ ions with larger radii exhibit more polarizability compared to the Li^+

ions and hence can more effectively stabilize O_2^- intermediates. Accordingly, NaO_2 can be formed as the stable discharge product in Na−O_2 cells, delivering lower charging overpotential.[3] Nonetheless, close thermodynamic stability of NaO_2 and Na_2O_2 results in formation of a diverse spectrum of products in this cell.[4,5] Therefore, detecting and understanding the physicochemical factors that control the composition of the products by affecting the thermodynamics or kinetics of the cell reaction is a priority in Na−O_2 cells.

2.1. Controlling the Discharge Products

2.1.1. Effect of Electrolyte. Chemical stability of the reaction intermediates (O_2^- in this case) plays a key role in controlling the composition and morphology of the discharge products in Li/Na−O_2 cells. The produced O_2^- radical with an unpaired electron in an aprotic environment is an active and unstable nucleophile and requires a stabilizing medium. It has been shown that Na−O_2 cells exhibit larger discharge capacities and micrometer-sized crystalline NaO_2 products in the presence of a protic additive like H_2O or weak acids.[6] In fact, protic additives in Na−O_2 cells function as a stabilizing medium for O_2^- by dissolving it into the aprotic electrolyte of the cell before combining with Na^+ and precipitating as NaO_2 (Figure 1a). A similar effect of protic additives in dissolving O_2^- intermediate into the cell electrolyte and promoting the growth of toroid Li_2O_2 has been reported for Li−O_2 cells.[7] On the other side, protic additives have detrimental effects on the cell performance by increasing the parasitic electrochemistry of the discharge products. Instead, a quantitative model developed in the latter study suggests that alternative additives with high Gutman acceptor and donor numbers (AN and DN) may facilitate the solution-mediated mechanism of product growth without deleterious effects of protic additives.

Similarly, the dissolved O_2^- intermediates were captured in electrolytes composed of solvents with relatively higher DN using in situ surface-enhanced Raman spectroscopy (SERS) on a gold electrode, whereas Na_2O_2 was detected in the solvents with lower DN.[8] Formation of Na_2O_2 in the low DN electrolytes has been correlated to the lower ability of the solvents to form an ion pair with O_2^- intermediates, resulting in further oxidation through a surface-mediated process. Effect of the electrolyte solvent on the morphology of products in Na−O_2 cells using a different approach showed that glyme-ethers with shorter chains promote the solution-mediated growth mechanism, while longer-chain ethers conduct the reaction toward a surface-mediated growth.[9] The authors related the observed lower discharge capacity and surface confined growth to the higher solubility of NaO_2 in the long-chain ethers, implying a contrast with Li−O_2 cells. However, effect of viscosity as well as solubility and diffusion rate of oxygen in different solvents on the electrochemical performance of the cells has not been considered in this inference. Moreover, a study on the correlation between the acid dissociation constant (pK_a) of the electrolyte solvents and the composition of discharge products in Na−O_2 cells confirmed the beneficial effect of the solvents with larger pK_a values toward the formation of NaO_2.[10] Furthermore, application of an electrolyte salt with higher DN has been suggested to increase the discharge capacity of Na−O_2 cells by enhancing the solution-mediated growth mechanism.[11]

2.1.2. Effect of the Moisture in Gas Phase. The presence of a trace amount of moisture in the gaseous oxygen fed into the Na−O_2 cells has a substantial effect on the composition of the discharge products and hence the overall performance of the cell. We noted that humidity has a more detrimental effect on the performance of Na−O_2 cells compared to Li−O_2, leading to formation of NaOH and Na_2CO_3 side products (Figure 1b).[12] The discharge capacity of Na−O_2 cells initially increases with increasing the humidity level in the cell atmosphere and decreases with further increase of the moisture. Formation of $Na_2O_2·2H_2O$ as the dominant product of the Na−O_2 cells discharged under humid conditions has been also reported.[13] The produced NaO_2 reacts with water to form $Na_2O_2·2H_2O$ and NaOH during the discharge, while formation of H_2O_2 is predicted to be more likely during the charge.[13] These studies highlight the importance of the cell design and experimental conditions on the composition of the discharge products in Na−O_2 cells.

2.1.3. Effect of the Air Electrode. Although the air electrode serves as the charge/mass transfer medium in Na−O_2 cells and is not directly involved in the electrochemical reaction of the cell, it may contribute to both the morphology and composition of the discharge products by affecting the reaction intermediates. In a study on the role of air electrode, NaO_2 was detected as the major product of Na−O_2 cells discharged using different carbonaceous air electrodes. However, no cubic product was observed on half of the discharged electrodes examined by SEM, indicating the effect of air electrode materials on the product morphology.[14] More recently, we revisited the effect of air electrode with special attention to the role of oxygen-containing functional groups at the electrode surface.[15] The presence of functional groups at the air electrode surface was found to substantially change the morphology and composition of the discharge products. While cubic crystalline NaO_2 was formed on hydrophobic electrodes, a conformal film of amorphous products was obtained in the presence of functional groups on hydrophilic electrodes (Figure 1c).

In addition, more positive ORR potential seen in the case of hydrophilic air electrodes suggests distinct electrochemical reaction paths on different electrodes. The presence of oxygen-containing functional groups may catalyze ORR by facilitating the oxygen adsorption at the air electrode surface, resulting in formation of peroxide-like products via a surface-mediated mechanism. Moreover, the air electrodes with different surface properties exhibit opposite responses toward the protic additives in the cell electrolyte. While addition of water into the cell electrolyte increases the discharge capacity of the cells employing hydrophobic electrodes, a reverse effect was observed on the hydrophilic air electrodes.[15] Reduction of water on the hydrophilic air electrodes results in formation of insulating side products on the electrode surface, which in turn increases the OER overpotential, whereas higher overpotential required for reduction of water on the hydrophobic air electrodes favors ORR and increases the discharge capacity by increasing the solubility of O_2^-. Accordingly, special attention should be given toward the experimental conditions as well as choosing the air electrode to thoroughly control the discharge products in Na−O_2 cells. The substantial effect of the air electrode combined with the presence of an uncertain amount of moisture in different studies is most likely responsible for most of the product diversity reported in Na−O_2 cells.

2.2. Discharge/Charge Mechanism

Understanding the mechanism behind the formation and growth of the large NaO_2 cubes as the preferable low-

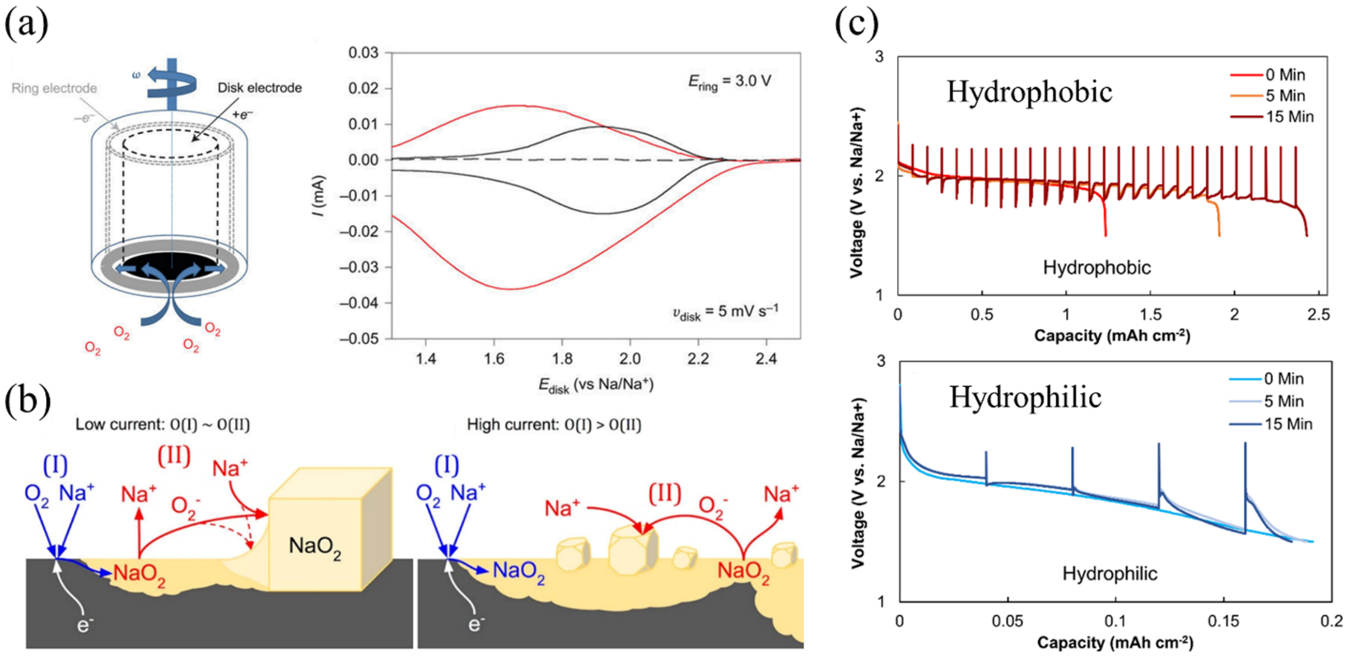


Figure 2. RRDE analysis of O_2^- intermediates in the cell electrolyte in the absence or presence of water[6] (a) (Reproduced with permission from ref 6. Copyright 2015 Nature Publishing Group), schematic of proposed mechanism for discharge process (b) (Adapted from ref 18. Copyright 2017 American Chemical Society), discharge curves for hydrophobic and hydrophilic air electrodes using regular constant current mode (0 min rest time) as well as GITT mode with different rest times (c) (Reproduced from ref 15. Copyright 2017 American Chemical Society).

overpotential discharge product in Na−O_2 cells may give clearer insight toward the control of discharge products. The main question herein is whether the NaO_2 cubes are formed by dissolution of O_2^- intermediates followed by NaO_2 precipitation or by continuous growth of nuclei via direct ORR at the surface of the cubes. There is enough evidence implying the presence of dissolved O_2^- in the cell electrolyte, which confirms the former solution-mediated mechanism. A rotating ring disk electrode (RRDE) study displayed higher disk and ring currents in the electrolyte containing 500 ppm added water compared to the dry electrolyte (Figure 2a), suggesting the increased dissolution of O_2^- in the presence of water.[6] More evidence was also obtained using quantitative measurement of the paramagnetic O_2^- using electron spin resonance (ESR) spectroscopy during the discharge and charge cycles.[16] ESR signal showed an increasing trend at the beginning of the discharge, which displays the increasing concentration of the dissolved O_2^-. By preceding the discharge, ESR signal showed a threshold where the nucleation of NaO_2 on the air electrode starts. A reverse solution-mediated mechanism was also proven to occur during the charge cycle. Moreover, theoretical calculations indicated an insulating character for NaO_2, implying that ORR should occur at the air electrode surface rather than NaO_2 particles.[17]

Although both experimental and theoretical studies demonstrate a solution-mediated mechanism for formation and decomposition of Na−O_2, some aspects of NaO_2 formation and decomposition remain unclear. For instance, rapid increase of overpotential results in premature capacity termination on discharge and low Coulombic efficiency on charge, which compromises the cycling performance of the cells. Several factors appear to be responsible for restricting the discharge and charge capacities. A combination of pore clogging by large NaO_2 cubes and the passivation of the electrode surface by a conformal film of product has been proposed by Nichols and McCloskey as limiting factors on discharge at low and high current densities, respectively (Figure 2b).[18] In addition, a combined surface/solution-mediated mechanism with a relative extent depending on the current density was also suggested by the authors.

Meanwhile, the surface characteristics of the air electrode demonstrate a significant influence on the growth mechanism too. Our recent study illustrated that the presence of oxygen-containing functional groups at the air electrode surface restricts the discharge capacity by conducting the growth mechanism toward a surface-mediated regime.[15] By contrast, cells employing hydrophobic air electrodes showed significantly larger capacities through a solution-mediated mechanism. Moreover, hydrophobic air electrodes exhibited increased discharge capacities with increasing rest time when discharged under the galvanostatic intermittent titration technique (GITT), while hydrophilic air electrodes displayed similar capacities (Figure 2c). These results indicate the mass transfer as a limiting factor for discharge capacity in a dominant solution-mediated regime. An equilibrium between the dissolving O_2^- and precipitating NaO_2 appears to control the discharge process. The discharge overpotential increases once the dissolving rate of O_2^- exceeds the precipitating rate of NaO_2. Therefore, increasing the resting time in GITT decreases the O_2^- concentration in the electrolyte and postpones the oversaturation potential drop, resulting in longer discharge time. Accordingly, the experimental factors affecting the solubility of O_2^- in the cell electrolyte are expected to alter the discharge mechanism. The presence of protic additives with high DN in the cell electrolyte as well as the surface properties of the air electrode material are among the most significant factors in this regard.

2.3. Side Reactions at Positive Electrode

Compared to Li−O_2, the electrochemical reaction occurring in Na−O_2 cells is purer to some extent, mainly owing to the

DOI: 10.1021/acs.accounts.8b00139
Acc. Chem. Res. XXXX, XXX, XXX−XXX

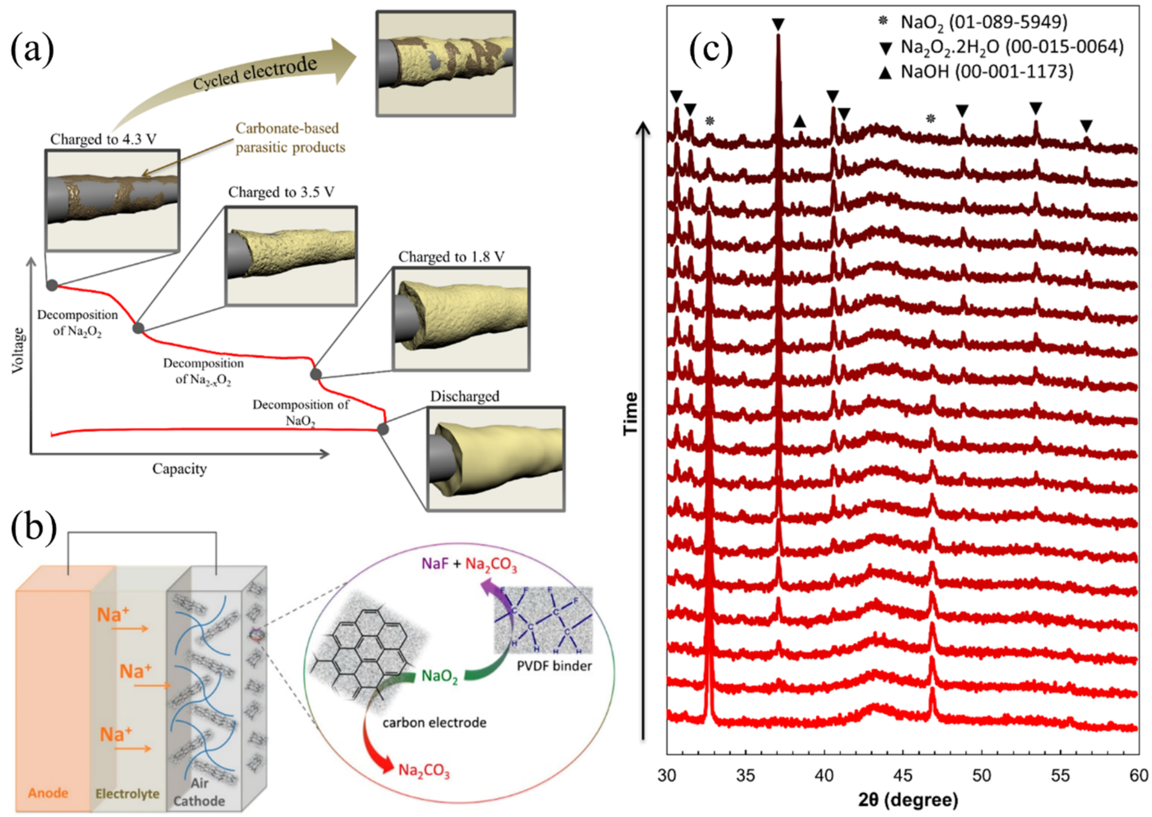


Figure 3. Schematic diagram of the Na−O_2 cell cycling mechanism (a) (Reproduced from ref 4. Copyright 2015 American Chemical Society), illustration of NaO_2 instability against carbon and PVDF binder (b) (Reproduced from ref 20. Copyright 2017 American Chemical Society), consecutive in-line XRD patterns for air electrodes discharged in a Na−O_2 cell (c) (Reproduced from ref 15. Copyright 2017 American Chemical Society).

higher capability of Na^+ to stabilize the O_2^- intermediates. The soft Lewis base O_2^- produced during the discharge reaction is more efficiently stabilized by a softer Lewis acid like Na^+ compared to Li^+. Thus, a lower amount of side products has been reported in the first discharge/charge cycle of Na−O_2 cells.[19] However, an increasing charging overpotential was observed during the consecutive cycling of the cell using a high-surface area carbonaceous air electrode.[4] Besides, analysis of the cycled electrode using X-ray absorption spectroscopy (XAS) illustrated the formation and accumulation of carbonate-based side products at the air electrode surface (Figure 3a). Like Li−O_2 cells, decomposition of the cell electrolyte as well as the carbonaceous air electrodes are assumed to be accountable. Meanwhile, a study using nuclear magnetic resonance (NMR) spectroscopy confirmed the formation of Na_2CO_3 because of solid-state reaction between NaO_2 and carbon electrodes (Figure 3b).[20]

Decomposition of NaO_2 in the presence of the cell electrolyte has been also proved as a potential source of side products in Na−O_2 cells by several studies.[21,22] $Na_2O_2{\cdot}2H_2O$ has been mostly reported as the aging product of the cells in the presence of ether-based electrolytes using X-ray diffraction (XRD) technique. We monitored the decomposition of the electrochemically formed NaO_2 using XRD, where $Na_2O_2{\cdot}2H_2O$ was appeared within only 1 h and continually increased afterward (Figure 3c).[15] A similar experiment using NMR spectroscopy showed a same time-dependent formation of side products, except that Na_2CO_3 was detected as the major decomposition product. Na_2CO_3 is likely formed in a noncrystalline form, which cannot be detected by XRD, while the ^{23}Na spectrum of $Na_2O_2{\cdot}2H_2O$ overlaps with the other product line shapes. In addition, formation of sodium acetate, formate, and carbonate has been reported for the soaked NaO_2 in dimethoxyethane (DME) for 15 days.[23] Similar side products were also found in the cells employing a diglyme-based electrolyte.[24] These findings strongly suggest that NaO_2 is not stable against the cell electrolyte as well as the carbonaceous materials, resulting in the formation of side products, which compromises the cycling performance of the cells. Stabilization of the cell electrolyte and the air electrode against NaO_2 is a priority to achieve reversible Na−O_2 cells.

2.4. Effect of Solid-State Catalysts

Solid-state catalysts can be applied to stabilize the oxidative discharge products in alkali metal−O_2 cells and simultaneously function as a protective shell for the carbonaceous air electrodes. Moreover, catalysts can significantly change the morphology of the discharge products by affecting the reaction intermediates.[2] Therefore, the role of the catalysts in these cells is slightly different from its classical definition. To elucidate the catalytic activity, we applied a specifically designed high-surface area catalyst composed of mesoporous Mn_3O_4 decorated with Pd nanoclusters in Li/Na−O_2 cells.[25] The special design of the catalyst with large surface to bulk ratio enabled the monitoring of chemical changes during the discharge/charge processes. XAS studies revealed a dynamic electron transfer between the catalyst and the discharge products (Figure 4a). Besides, analysis of the discharge products showed higher content of oxygen-rich products on the catalyst surface. Accordingly, the catalytic activity in Li/Na−O_2 cells can be correlated to the

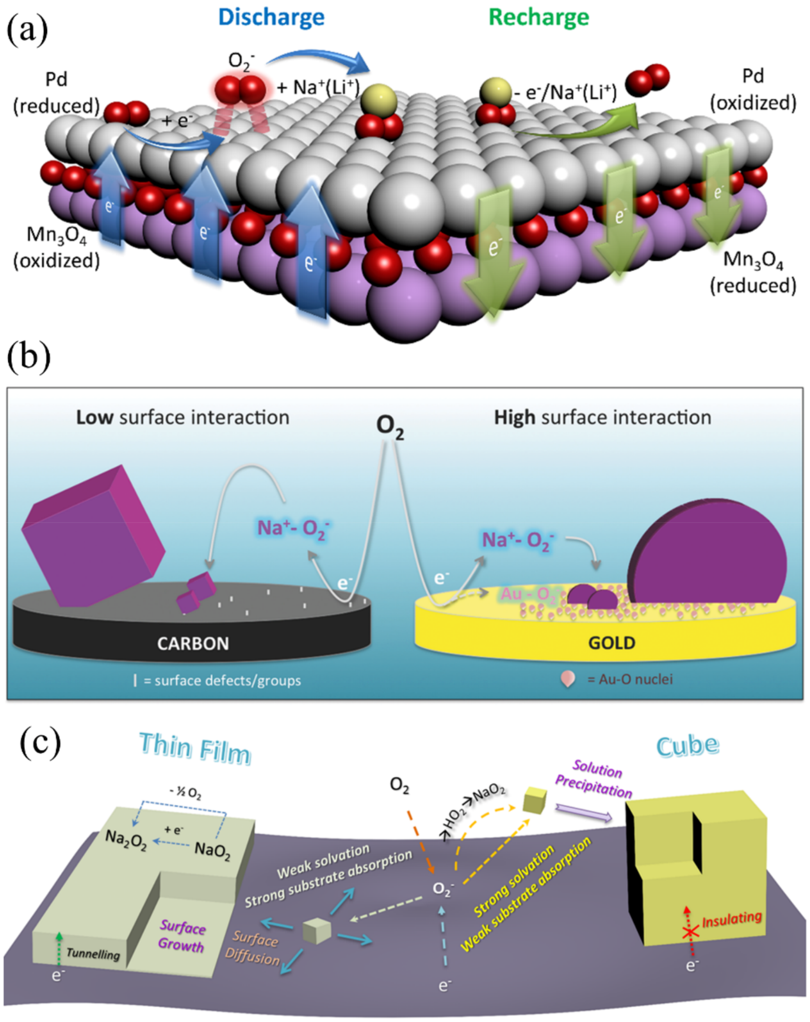


Figure 4. Schematic diagram of catalytic mediated reaction mechanisms in $Na-O_2$ cells on Mn_3O_4/Pd[25] (a), Au/carbon[26] (b), and $CNT@Co_3O_4$[27] (c) surfaces. Images adapted with permission from (a) ref 25 (copyright 2017 Royal Society of Chemistry), (b, c) refs 26 and 27 (copyright 2017 Wiley-VCH).

ability of the catalyst to stabilize the O_2^- intermediates at the electrode surface, which also explains the morphology changes. This ability of the catalyst may also benefit the cell electrolyte by reducing the electron density on the products, which results in decreased decomposition of the electrolyte through nucleophilic attacks.

Another function of the catalysts in $Li/Na-O_2$ cells involves controlling the morphology of the products by affecting the reaction intermediates. The latter role was recently highlighted by comparing the Au and carbon air electrodes in $Na-O_2$ cells.[26] The Au electrode exhibited lower discharge capacity with flake-like NaO_2 compared to the carbon electrode with typical cubic product. The high surface energy and affinity of the Au surface toward O_2/O_2^- has been mentioned as the origin of the electrode activity (Figure 4b). Similar to the hydrophilic surfaces, high O_2^- affinity of the electrode conducts the growth mechanism to a surface-mediated regime, resulting in formation of conformal film of products.[15] An analogous effect of the electrode surface on the morphology of the products in $Na-O_2$ cells was observed in our earlier study using atomically deposited Co_3O_4 catalyst (Figure 4c).[27] Furthermore, application of catalysts with high surface energy may increase the Coulombic efficiency of the cells by reducing the O_2^- crossover toward the separator and negative electrode. The O_2^- crossover issue is discussed in detail in the next section.

3. O_2/O_2^- CROSSOVER AND DENDRITE FORMATION AT SODIUM ELECTRODE

Higher stability/solubility of $Na^+-O_2^-$ intermediates in the cell electrolyte compared to its Li counterpart may benefit $Na-O_2$ cells by increasing the discharged capacity due to the solution-mediated growth mechanism. However, the dissolved reaction intermediates may migrate toward separator and metallic Na because of concentration gradient in the electrolyte. The migrated intermediates may then precipitate on the non-conductive separator.[6,28] Accordingly, the O_2^- crossover decreases the Coulombic efficiency of the cell due to the formation of segregated products, which cannot be recovered on charge. Moreover, a portion of crossed O_2^- may reach the metallic Na, resulting in formation of an insulating oxide layer on the Na surface. Our recent results demonstrate that the discharge capacity in $Na-O_2$ cells may be restricted by increased ORR overpotential on the negative Na electrode. The air electrode design should be optimized to minimize the O_2/O_2^- crossover issue.

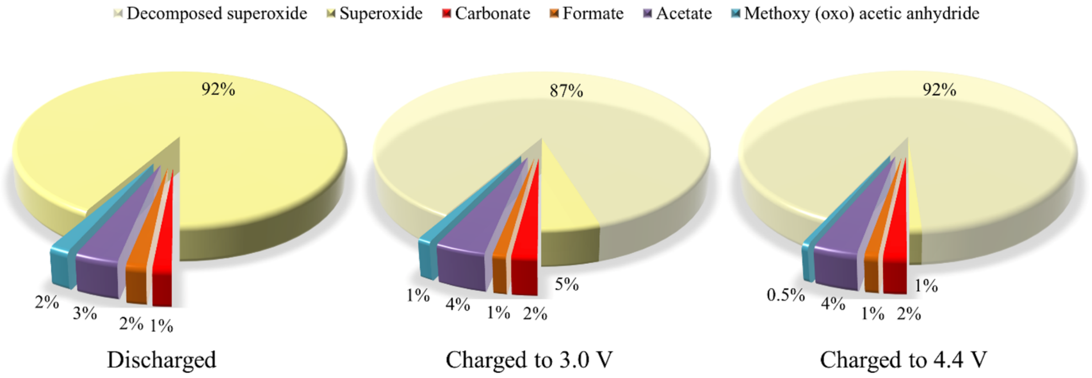


Figure 5. Quantitative analysis of the decomposition products formed in Na$-$O$_2$ cells at different stages of discharge and charge. Image reproduced with permission from ref 24. Copyright 2016 Wiley-VCH.

Formation of dendrite structures on the metallic Na during the charge cycle is another fundamental challenge facing the development of Na$-$O$_2$ cells even at the laboratory scale. Multiple mechanisms have been proposed to explain the dendrite formation on the metallic electrodes including the formation of an inhomogeneous solid electrolyte interface (SEI) or a concentration gradient at the electrode/electrolyte interface. It has been shown that dendrite formation may affect the electrochemical reaction of Na$-$O$_2$ cells from the first cycle by short-circuiting the cell at the early stages of charge.[29] Visual inspection of a Na/Na cell using optical imaging demonstrated the formation and growth of dendritic Na structure specially at relatively higher current densities.

Different strategies have been employed to tackle the dendrite formation and protection of metallic Na electrodes including interface engineering, electrolyte modification, and electrode architecture.[30] Among them, applying an ultrathin protective layer that is permeable to the corresponding metallic ions may form a homogeneous artificial SEI layer on the electrode surface and hence mitigate the dendrite formation. To form such an artificial SEI layer, an ultrathin Al$_2$O$_3$ coating was directly deposited on the metallic Na electrode using atomic layer deposition (ALD) technique.[31] The resultant electrode showed a stable cycling performance at high current densities in Na/Na cells. To further increase the stability of the metallic Na electrode, an inorganic$-$organic coating formed by consecutive deposition of trimethylaluminum and glycerol was developed via molecular layer deposition (MLD) in our group.[32] The added organic component in the coating layer significantly improved the Na cycling life by increasing the flexibility of the protective coating against the large volume changes.

The electrolyte anions have also been shown to influence the stability of the metallic Na (at least in weakly solvating solvents) by affecting the SEI layer.[33] Na$-$O$_2$ cells discharged using sodium trifluoromethanesulfonimide (NaTFSi) in DME exhibited the lowest discharge capacity, while NaPF$_6$ showed the best performance. Formation of a stable NaF film on the metallic Na in the presence of PF$_6^-$ anion is mentioned to explain the improved performance. The influence of the electrolyte anions on the SEI has been correlated to their chemical structure. However, the role of salt DN in stabilizing and conducting the O$_2^-$ intermediates toward the negative electrodes should not be underestimated. Our knowledge about the negative electrode in Na$-$O$_2$ cells is limited to a few reports in the literature, and more fundamental studies are required.

4. SIDE REACTIONS RELATED TO THE CELL ELECTROLYTE

Instability of organic electrolytes in the highly oxidative environment of Li$-$O$_2$ cells has been extensively studied.[34] In comparison to Li$-$O$_2$, higher chemical stability of the reaction intermediates in Na$-$O$_2$ cells results in less decomposition and side products.[19] Nonetheless, oxidative decomposition of the cell electrolyte, as well as the carbonaceous air electrodes to a lesser extent, also occurs in Na$-$O$_2$ cells. Analysis of the side products in Na$-$O$_2$ cells using diglyme electrolyte revealed the formation of sodium acetate, formate, and carbonate as the dominant decomposition products (Figure 5).[24] A mechanism based on hydrogen abstraction from ether-based electrolytes by O$_2^-$ is known to form the detected side products. Moreover, formation of singlet oxygen (^{1}O$_2$) during the electrochemical reaction of Na$-$O$_2$ cells is also shown to be accountable for formation of side products.[35]

Accumulation of the formed side products in consecutive cycles in Na$-$O$_2$ leads to cell failure, since the side products cannot be decomposed within the narrow NaO$_2$ decomposition window, whereas the large overpotential required for Li$_2$O$_2$ decomposition in Li$-$O$_2$ cells increasingly intensifies the decomposition of the cell electrolyte and the air electrode. Despite the slight difference between the failure mechanisms, instability of the available organic electrolytes is the primary limiting factor for cycling performance in both Li and Na$-$O$_2$ cells. An electrolyte with higher stability against O$_2^-$ is required to further enhance the cyclability of the cells. Nevertheless, the lower charging overpotential makes the electrolyte search more promising in the case of Na$-$O$_2$ cells.

5. CONCLUSIONS AND OUTLOOK

High-energy density Li/Na$-$O$_2$ cells are considered as a promising solution to the void in electrochemical energy storage systems, especially for electric transportation purposes. However, the high energy density in Li$-$O$_2$ cells comes with a large charging overpotential, which causes a variety of fundamental obstacles toward its practical development. Meanwhile, Na$-$O$_2$ cell displays a smoother development pathway owing to its reversible superoxide chemistry. Despite some common challenges and similar working principles, Na$-$O$_2$ cells exhibit a distinct electrochemical mechanism and unparalleled challenges compared to their Li counterparts. Instability of the available electrolyte solvents is agreed upon as the foremost challenge, which compromises the cycling performance in both cells. Nonetheless, the research on other

DOI: 10.1021/acs.accounts.8b00139
Acc. Chem. Res. XXXX, XXX, XXX$-$XXX

components of Na–O_2 cells is more controversial mainly because of the high chemical reactivity of the sodium and its oxides. Therefore, excessive cautions should be taken to design the experiments and interpret the results in this battery system.

Controlling the discharge products and elucidating the effective physicochemical factors to obtain NaO_2 as the dominant product is essential to sustain a low charging overpotential as the key advantage of Na–O_2 over Li–O_2 cells. The nature of the air electrode/electrolyte interactions should be precisely studied in this regard. Such interactions not only affect the chemical composition of the products but also influence the morphology by conducting the growth mechanism. The air electrodes with lower surface energy exhibit lower interactions with reaction intermediates and thus invigorate the solution-mediated mechanism, resulting in increased discharge capacity. On the other side, a solution-mediated mechanism carries the reaction intermediates through the separator and over to the metallic Na. The carried over intermediates then passivate the Na surface, which in turn can restrict the discharge capacity of the cell. Moreover, the reduced intermediates at the negative electrode as well as the electrically isolated products precipitated on the separator cannot be recovered on charge. Therefore, the increased discharge capacity in a solution-mediated mechanism comes at a cost of lower Coulombic efficiency.

In contrast, air electrode materials with higher surface energy more efficiently stabilize the reaction intermediates at the electrode surface and reduce the crossing over of the intermediates. However, a surface-mediated mechanism blocks the accessible reactions sites and reduces the discharge capacity. Designing the air electrodes with high surface energy and acceptable discharge capacity should be perused in this regard. Furthermore, the Na electrode passivation may restrict the discharge capacity and decrease the energy efficiency of the cell by imposing overpotential on discharge and charge. More fundamental studies are required to understand the reactions occurring on the negative electrode of Na–O_2 cells. Besides, innovative solutions are needed to suppress the dendrite formation on the Na surface as well as to protect the highly reactive metallic electrode in the harsh environment of the cell. Addressing the mentioned obstacles will illuminate the prospect ahead for Na–O_2 development.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: xsun@eng.uwo.ca.

ORCID

Hossein Yadegari: 0000-0002-2572-182X
Xueliang Sun: 0000-0003-2881-8237

Notes

The authors declare no competing financial interest.

Biographies

Hossein Yadegari received his B.Sc. in Chemistry from Sharif University of Technology and Ph.D. in Materials Engineering from University of Western Ontario (UWO). His main research interests are associated with energy conversion and storage, electrochemistry of nanomaterials, and electrocatalysis. His current research is focused on developing in-operando spectroscopic techniques to study alkali metal–oxygen cells.

Xueliang (Andy) Sun is a Senior Canada Research Chair (Tier 1) and a Full Professor at the University of Western Ontario. He received his Ph.D. in Materials Chemistry in 1999 at the University of Manchester, U.K., followed by work as a postdoctoral fellow at the University of British Columbia and as a Research Associate at l'Institut National de la Recherche Scientifique (INRS). His current research interests are associated with synthesis of advanced nanomaterials for electrochemical energy storage and conversion including lithium ion batteries, solid-state batteries, metal–air batteries, and PEM fuel cells.

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