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# Aprotic Alkali Metal—O<sub>2</sub> Batteries: Role of Cathode Surface-Mediated Processes and Heterogeneous Electrocatalysis

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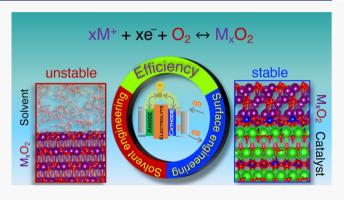


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ABSTRACT: Alkali metal— $O_2$  batteries (i.e., Li/Na— $O_2$ ) with high specific energies are promising alternatives to state-of-theart metal-ion batteries. However, they are plagued by challenges arising from the underlying redox chemistry, resulting in reduced efficiencies. These challenges for Li/Na— $O_2$  batteries stem from the nature of the interface between solid discharge product(s) and either (i) the aprotic electrolyte or (ii) the solid cathode. In the former, the reactive nature of the solid/liquid interface leads to chemical disproportionation of the discharge product(s) and the electrolyte, while in the latter, the presence/lack of atomistic interactions at the solid—solid interface leads to large overpotential losses (>1 V) during charging. Approaches to overcome these challenges would involve



decoupling these factors. For instance, the use of inert aprotic electrolytes would facilitate catalytically driven, surface-mediated discharge product(s) growth, providing avenues to use cathode surface modifications as levers to enhance voltaic efficiency and discharge product stability, resulting in improved performance.

protic alkali metal $-O_2$  (M $-O_2$ ; M = Li, Na) batteries have the potential to overcome the limitations associated with the current-generation energy storage technologies because of their high specific energies (energy per unit mass). 1-6 This capability largely stems from the difference in the energy storage mechanisms between M-O2 batteries and state-of-the-art alkali metal-ion batteries. The latter largely rely on intercalation-based chemistries, with the driving force arising from the difference in the chemical potential of the metal ions in the interstitials of the anodic and the cathodic materials. On the other hand, M-O<sub>2</sub> batteries take advantage of the electrochemical redox transformations of electronegative molecular oxygen with electropositive alkali metal cations, similar to regenerative proton-based fuel cells.<sup>7,8</sup> These batteries consist of an alkali metal anode, an alkali metal salt dissolved in an aprotic solvent as the electrolyte, and generally a porous carbon-based cathode, as shown in Figure 1a. During discharge, the alkali metal anode is oxidized  $(M \rightarrow M^+ + e^-)$ , followed by transport of the M<sup>+</sup> ions through the electrolyte to the cathode, where they reduce O2 (oxygen reduction reaction, ORR) in the presence of electrons (circulated through an external circuit from the anode) to form solid  $M_xO_2$  ( $1 \le x \le$ 2) species.<sup>1,9</sup> These processes are reversed during the charge cycle, resulting in the oxygen evolution reaction (OER) and redeposition of the alkali metal onto the alkali metal electrode.

The reaction free energy for the conversion of M and  $O_2$  to form  $M_xO_2$  ( $1 \le x \le 2$ ) is the source of energy storage for M— $O_2$  batteries. The theoretical specific energies of various aprotic battery systems are depicted in Figure 1b, clearly indicating that M— $O_2$ -based technologies hold significant promise to substantially alter the energy storage landscape as compared to the state-of-the-art Li-ion batteries. Although the practical specific energy of aprotic M— $O_2$  batteries still remains challenging to define, attaining  $\sim$ 40—60% of the theoretical specific energy would result in target-specific energies in the range of 900—1400 Wh-kg<sup>-1</sup>, which represents a 3- to 4-fold improvement in energy storage as compared to the current-generation Li-ion batteries. Consequently, these technologies, with higher specific energies, are well suited to meet the ever-

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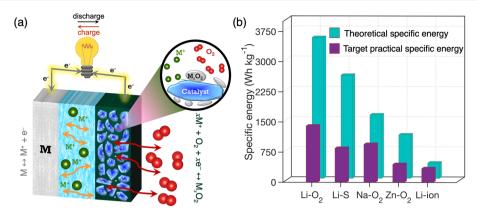


Figure 1. (a) Schematic representation of an aprotic  $M-O_2$  battery composed of an alkali metal anode, an aprotic electrolyte, and a cathode, showing the reversible formation of solid  $M_xO_2$  species during discharge and charge cycles, respectively. (b) Target and theoretical specific energies of the next-generation battery technologies in comparison to the state-of-the-art Li-ion batteries.

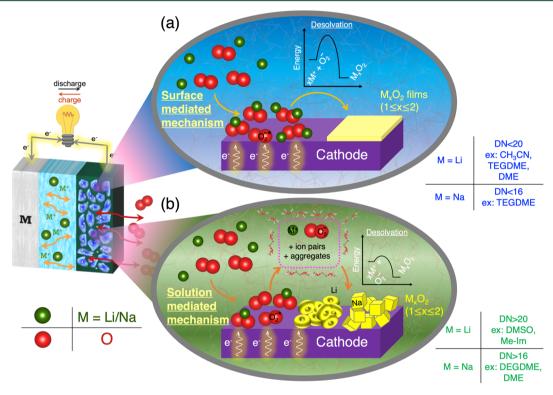


Figure 2. Mechanisms of  $O_2$  reduction in  $M-O_2$  batteries (M=Li, Na) resulting in the formation of solid discharge  $M_xO_2$  ( $1 \le x \le 2$ ) species during discharge. (a) Surface-mediated growth of discharge species stemming from either endergonic solvation or high barriers to desolvation. (b) Solution-mediated growth of discharge species stemming from exothermic solvation or low barriers to desolvation. The adsorbed  $MO_2^*$  or  $O_2^{-*}$  species are solvated in solution, followed by aggregation and subsequent precipitation on the electrode surface upon saturation.

increasing need for higher energy storage and enhance the overall performance of future technologies, such as electric vehicles, space exploration technologies, and other stationary storage applications. However, the very nature of the chemical conversions that lead to high specific energy results in a number of challenges, including large overpotential losses ( $\eta > 1$  V) during the charge cycle and instability of the discharge products, giving rise to parasitic side reactions. These challenges have resulted in poor cyclability and hampered the practical application of these devices. In this Perspective, approaches to fundamentally address these issues in the most commonly implemented aprotic M–O<sub>2</sub> batteries, such as Li/Na–O<sub>2</sub>, will be analyzed. We will focus primarily on progress

in the development of  ${\rm Na-O_2}$  batteries, motivated by the limited number of studies on these systems and their significant potential to serve as earth-abundant energy storage devices.

The mechanisms of formation of the solid discharge products that store the electrical energy in aprotic  $M-O_2$  batteries are highly complex. Numerous studies have synergistically combined electrochemical and characterization tools to investigate the effect of different mechanisms on the discharge product formation, and they have subsequently correlated these effects to the overall attained capacity, as well as to the charge overpotential losses. It has been reported that, during discharge, solid  $M_xO_2$  (M = Li, Na;  $1 \le x \le 2$ )

products are formed either via (i) direct electrochemical reduction of O<sub>2</sub> in the presence of electrons and M<sup>+</sup> ions on the surface of the cathode (surface-mediated) or (ii) initial electron reduction of O2 on the surface to form surfaceadsorbed MO<sub>2</sub>\* or O<sub>2</sub>\*, followed by dissolution of adsorbed MO<sub>2</sub>\* or O<sub>2</sub><sup>-\*</sup> as M<sup>+</sup> and O<sub>2</sub><sup>-</sup> ions, respectively, which then aggregate in the solution and finally reprecipitate upon saturation as solid M<sub>x</sub>O<sub>2</sub> products on the cathode surface (solution-mediated), as illustrated in Figure 2.  $^{13-16}$  The nature of the discharge mechanism has been attributed to the inherent properties of the solvent used in the electrolyte, as well as the potential of operation. <sup>13,16–18</sup> For instance, a combination of operando surface-enhanced Raman spectroscopy (SERS) and rotating ring disk electrode (RRDE) studies showed that the donor number (DN) of the solvent (in kcal/mol) is a critical parameter for differentiating between solution- and surfacemediated mechanisms for the formation of  $\text{Li}_x \text{O}_2$   $(1 \le x \le 2)$ species in Li-O2 batteries, as illustrated in Figure 2. This phenomenon is based on the fact that the solvent DN drives the equilibrium between the cathode surface-adsorbed species (LiO<sub>2</sub>\* or O<sub>2</sub>\*) and the corresponding ions (Li<sup>+</sup> and O<sub>2</sub>). This equilibrium is, in turn, primarily dictated by the energetics associated with solvation of the cathode surface-adsorbed species (LiO<sub>2</sub>\* or O<sub>2</sub>-\*) and the desolvation of the ions in solution:

$$\text{LiO}_{2}^{*} \leftrightarrow \text{Li}_{(\text{sol})}^{+} + \text{O}_{2(\text{sol})}^{-} + \text{ion pairs}$$

$$+ \text{ higher aggregates (clusters)}$$
(1)

Among the different DN solvents used in Li-O<sub>2</sub> systems, it has been generally observed that, for solvents with a DN < 20 (for example, tetraethylene glycol dimethyl ether (TEGDME), dimethoxyethane (DME), and acetonitrile (CH<sub>3</sub>CN)), the electrode surface-mediated mechanism for discharge product formation dominates due to the endergonic Gibbs free energy change  $(\Delta G)$  associated with the solvation of LiO<sub>2</sub>\* (eq 1) or  $O_2^{-*}$ . This results in the initial formation of film-like structures (either LiO<sub>2</sub> or Li<sub>2</sub>O<sub>2</sub> from further electrochemical reduction of  $LiO_2$  via  $LiO_2^* + Li^+ + e^- \rightarrow Li_2O_2$ ) on the cathode surface (Figure 2a), which in turn provide a platform for further nucleation and growth of extended solid structures. 13 In this scenario, the chemical and structural nature of the solid discharge products can be controlled by tuning their interaction with the cathode surface, via geometric and electronic effects, through the introduction of an electrocatalyst. 19-26 These templates can then be used for extended growth of discharge species up to ~18-30 nm thick. Such a scenario can lead to reduced charge overpotential losses ( $\eta$  < 1.0 V), <sup>20,22,26</sup> albeit sometimes at the cost of lower discharge capacity due to changes in the chemical nature of the discharge products or challenges with controlling the nucleation of the solid discharge product on the electrocatalyst surface as the thickness of the discharge product increases.<sup>27</sup> In the case of electrolytes with solvent DN > 20 (for example, dimethyl sulfoxide (DMSO), 1-methylimidazole (Me-Im)), a solutionmediated mechanism dominates, wherein the surface-adsorbed  $\text{LiO}_2^*$  or  $\text{O}_2^{-*}$  species solvate into the electrolyte as  $\text{Li}^+$  and  $\text{O}_2^-$  aggregates (exothermic  $\Delta G$  for eq 1). The solvated  $\text{Li}^+$  and O<sub>2</sub> (sol) aggregates undergo chemical combination to Li<sub>2</sub>O<sub>2</sub> and consequently reprecipitate upon saturation on the cathode surface as solid crystals of Li<sub>2</sub>O<sub>2</sub>, as illustrated in Figure 2b. 13 The formation of micrometer-sized, toroidal-shaped Li<sub>2</sub>O<sub>2</sub> structures in Li-O2 systems has been reported in the case of a solution-mediated mechanism, which provides advantages in terms of overall capacity.  $^{28,29}$  However, the formation of such extended toroidal  $\rm Li_2O_2$  structures results in high overpotential losses ( $\eta > 1.0$  V) during charging due to the insulating nature of  $\rm Li_2O_2$ . This has been addressed to some extent by the use of homogeneous catalysts in the form of redox mediators or solution-based additives (for example, tetrathiafulvalene, 2,5-di-tert-butyl-1,4-benzoquinone (DBBQ), and anthraquinone).  $^{30-32}$  Another challenge with this mechanism is associated with the high reactivity of solvated  $\rm O_2$  anions, which can trigger irreversible parasitic side reactions.  $^{32,33}$ 

A dependence of the discharge mechanism on the applied potential has also been reported for Li–O $_2$  systems. It is generally observed that, at high potentials (low overpotential; >2.7 V vs Li/Li $^+$ ), a solution-mediated mechanism remains dominant in high DN solvents (>20), but at lower potentials (high overpotential; <2.6 V vs Li/Li $^+$ ), it transforms into a surface-mediated mechanism. On the other hand, low DN solvents undergo a surface-mediated mechanism at almost all potentials of discharge due to the inherently low solubility of LiO $_2^*$  in the solvent.  $_{13,16}^{13,16}$ 

Similar studies have been extended to Na-O2 systems, with the primary difference being that the superoxide (NaO<sub>2</sub>) is the major discharge product. 14,15 RRDE and mass spectroscopy studies have shown that formation of NaO2 involves a oneelectron transfer process  $(Na^+ + O_2 + e^- \rightarrow NaO_2)$ . <sup>14</sup> Analogous to  $\text{Li-O}_2$  batteries, the solvent DN has been shown to affect the mechanism of discharge product formation, as illustrated in Figure 2. It is interesting to note that, somewhat differently from the case of Li-O2 systems, even solvents with a DN of ~18-20 (for example, DME and diethylene glycol dimethyl ether (DEGDME)) result in a solution-mediated growth of cube-like NaO2 structures. The solvation of surfaceadsorbed  $NaO_2^*$  or  $O_2^{-*}$  in these systems is hypothesized to be facile even for such low DN solvents, while the desolvation barrier associated with Na<sup>+</sup>-O<sub>2</sub><sup>-</sup> agglomerates to precipitate as NaO<sub>2</sub> crystals has been hypothesized to dictate the underlying mechanism during discharge. 14,17 In the case of electrolytes with solvent DN  $\geq$  18, the desolvation of Na<sup>+</sup>-O<sub>2</sub> agglomerates is found to be facile, resulting in a solutionmediated growth of cube-like NaO2 crystals, as shown in Figure 2b. However, when electrolytes with solvent DN  $\leq$  16 (such as TEGDME) are used, the desolvation barrier for Na+-O<sub>2</sub> agglomerates to reprecipitate as NaO<sub>2</sub> crystals is found to be high, consequently resulting in a surface-mediated growth of NaO<sub>2</sub> (Figure 2a).<sup>14</sup> In general, the solvent DN plays a critical role in determining the mechanism of discharge product growth in M-O<sub>2</sub> (M = Li, Na) battery systems, with low or high DN solvents (the window of which is dependent on the nature of the discharge species) leading to a surface- or solution-mediated mechanism, respectively.

In general, the solvent donor number plays a critical role in determining the mechanism of discharge product growth in  $M-O_2$  (M=Li, Na) battery systems.

Among  $M-O_2$  batteries, Li-based ones have attracted the most interest over the past decade. However, with the wider availability of Na as compared to Li, Na $-O_2$  batteries have

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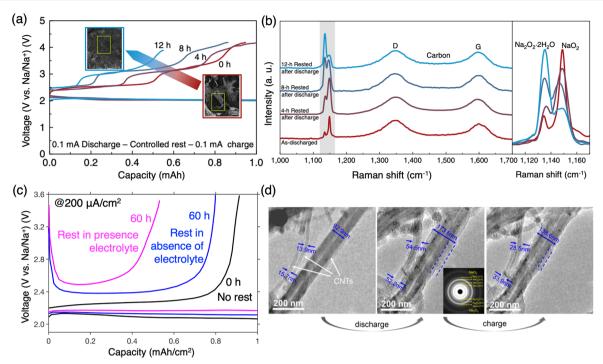


Figure 3. Instability of the discharge products in Na-O<sub>2</sub> batteries. (a) Galvanostatic discharge-charge profiles of Na-O<sub>2</sub> batteries as a function of cell resting time between the discharge and charge cycles. The insets show the scanning electron micrographs of the discharged cathodes as the resting time between discharge and charge was increased from 0 to 12 h. (b) Raman spectroscopy of discharged cathodes with varying resting times (0-12 h), indicating chemical disproportionation of NaO<sub>2</sub> to Na<sub>2</sub>O<sub>2</sub>·2H<sub>2</sub>O. Panels (a) and (b) are reprinted with permission from ref 36. Copyright 2016 Springer Nature. (c) Charge profiles of carbon-based Na-O<sub>2</sub> electrodes rested for 60 h after discharge under different conditions: in the presence of the electrolyte in an entire cell setup, or in the absence of the electrolyte when the cathode is isolated under Ar. Panel (c) is reprinted from ref 38. Copyright 2020 American Chemical Society. (d) *In situ* transmission electron micrographs of a carbon nanotube-based cathode showcasing formation and oxidation of NaO<sub>2</sub> (marked with dotted lines) during discharge and charge cycles, respectively. Panel (d) is reprinted with permission from ref 42. Copyright 2018 American Chemical Society.

recently gained considerable attention. <sup>34,35</sup> One of the main advantages of Na–O<sub>2</sub> systems is the observed low discharge and charge overpotential losses (<200 mV). This high cyclic efficiency has been attributed to the reversible formation of NaO<sub>2</sub> (Na<sup>+</sup> + e<sup>-</sup> + O<sub>2</sub>  $\leftrightarrow$  NaO<sub>2</sub>;  $E^0$  = 2.27 V vs Na/Na<sup>+</sup>) structures as the primary discharge product, with low kinetic barriers in commonly used electrolyte/electrode systems.

Despite the advantages of Na-O2 batteries in terms of the overall lower overpotential losses during cycling as compared to Li-O<sub>2</sub> ones, their performance is limited by two main factors: (i) the instability of the discharge product when the cell is rested (no applied current) between the discharge and charge cycles, and (ii) a significant increase in the charge overpotential toward the end of the charge cycle. The first challenge is clearly impractical for applications such as electric vehicles, wherein the battery is almost never charged immediately post discharge. Figure 3a shows the instability of the discharge product leading to shortening of the low charge overpotential regime/plateau (oxidation occurring below 2.5 V vs Na/Na<sup>+</sup>) as the resting time between the discharge and charge cycles of a Na-O2 battery cell is increased from 0 (charged immediately) to 12 h using a DEGDME based-electrolyte (DN = 18). The charge capacity obtained in the low overpotential regime (<2.5 V vs Na/Na<sup>+</sup>) is decreased by 5 times when the cell is rested for 12 h as compared to a cell that is charged immediately. To understand the underlying chemical processes that result in such charge behavior, spectroscopic and microscopic analyses of the discharged species have been conducted. Chemical disproportionation of NaO<sub>2</sub> to Na<sub>2</sub>O<sub>2</sub>·2H<sub>2</sub>O was fingerprinted using Raman spectroscopy (Figure 3b) with increasing resting time, accompanied by a loss of the cubic NaO<sub>2</sub> structures, as shown in the Figure 3a inset.<sup>36</sup> It is worth noting that the inherent H<sub>2</sub>O content of the solvent was <5 ppm, which is not sufficient to aid in such large-scale transformation of NaO<sub>2</sub> to Na<sub>2</sub>O<sub>2</sub>·2H<sub>2</sub>O. Therefore, the origin of H<sub>2</sub>O involved in this chemical disproportionation reaction was reported to stem from the proton abstraction from the organic solvent used in the electrolyte. The process of proton abstraction was hypothesized to occur via the reaction between solvated O<sub>2</sub> anions and high DN ( $\geq$ 18) organic solvents. The subsequent formation of Na<sub>2</sub>O<sub>2</sub>·2H<sub>2</sub>O from NaO<sub>2</sub> was hypothesized to cause an increase in the charge overpotentials beyond 2.5 V vs Na/Na<sup>+</sup>, as shown in Figure 3a. <sup>36,37</sup>

To further shed light on the factors that induce the instability of NaO<sub>2</sub> in Na-O<sub>2</sub> systems, Li and co-workers studied the charging behavior of DEGDME-based (DN = 18) cells rested for 60 h after discharge under two different conditions: (i) a cell containing all its components, including the electrolyte, and (ii) only the discharged cathode isolated under dry conditions (in Ar) in the absence of any electrolyte.<sup>38</sup> It was clearly observed (Figure 3c) that, when the electrode was rested after discharge in the absence of the electrolyte and reassembled in a cell, the charging potential was <2.5 V (V vs Na/Na $^+$ ) for  $\sim$ 70% of the total cell charge capacity (blue curve in Figure 3c). On the other hand, when the cathode was rested in a cell containing the electrolyte and all the cell components, the low overpotential regime at a

charging potential of <2.5 V (V vs Na/Na<sup>+</sup>) was observed for only 30% of the overall cell charge capacity (magenta curve in Figure 3c). These studies suggest that the solvent in the electrolyte played a critical role in the chemical disproportionation of NaO<sub>2</sub>, consequently resulting in an increase in overpotential losses. Similar conclusions were drawn by other studies. This highlights the fact that the intrinsic stability

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The second major challenge observed in Na-O2 systems is associated with the increase in the overpotential losses during the later stage of charging. An increase in the charging potential to >3.5 V (V vs Na/Na<sup>+</sup>) beyond 80% of the total cell charge capacity is observed in Figure 3, panels a and c (red and black curves), even in the cases when the cell was not rested. A potential cause for such behavior has been detailed in an in situ transmission electron microscopy (TEM) study by Sun and co-workers. 42 A carbon nanotube-based cathode in a Na-O<sub>2</sub> battery cell was systematically imaged during discharge and charge cycles, as shown in Figure 3d. It was observed that the carbon nanotube cathodes swelled in diameter during discharge due to the formation of bulk NaO2 crystals (blue dotted highlight in Figure 3d). This structural change was irreversible, and the initial geometry of the pristine carbon nanotubes was not fully recovered after completion of the charge cycle (blue dotted highlight in Figure 3d).<sup>42</sup> The incomplete oxidation was hypothesized to result from the discharge product present near the surface of the carbon nanotubes, which was characterized to be a mixture of NaO2 and Na<sub>2</sub>O<sub>2</sub> using electron diffraction measurements. These findings suggested that the rise in overpotential observed in the later stage of charging in Na-O2 batteries could be potentially associated with a residual mix of discharge products in close proximity to the electrode surface. While these findings are insightful, extrapolation to other electrode materials is not trivial, given that the observed phenomena could have been induced by the geometrical constraints arising from the inherent structure of the carbon nanotubes used in the study. Hence, the insights drawn from these studies clearly advocate for the need to investigate the underlying processes taking place at different interfaces present in a Na-O2 cell, such that the challenges associated with (i) the instability of the discharge product and (ii) the observed high overpotential losses in the later stage of charging can be mitigated.

To effectively mitigate the challenges associated with Na—O<sub>2</sub> batteries, there is a need to critically understand the underlying processes that occur at the electrolyte—discharge product and the discharge product—cathode interfaces. In the first case, the overarching goal would be to identify electrolytes that are inert and do not react with the discharge product, NaO<sub>2</sub>. To this end, some research has been conducted to understand the role of the electrolyte in these systems, which

has led to modifications of the commonly used electrolytes. For instance, altering the salt concentration in the electrolyte can cause a direct change in (i) the nature of the salt-solvent coordination structure and the interaction with the discharge product, and (ii) the chemical and electrochemical stability of the solvent. 43 More recently, Suo and co-workers have introduced the concept of "solvent-in-salt" type electrolytic systems, consisting of a large concentration of salt in a limited amount of solvent for Li-sulfur batteries. 44 Such an approach has resulted in the minimization of free solvent molecules in the electrolyte, consequently decreasing the probability of interaction of the discharge products with the solvent molecules. 44,45 This approach has been extended to Na-O<sub>2</sub> batteries by increasing the salt concentration (Na<sup>+</sup> ion concentration) in the electrolyte to lower the rate of disproportionation of the discharge product. 41,46,47 However, it is also worth noting that the increase in the salt concentration results in higher viscosity, causing lower (i) ionic conductivity and (ii) oxygen solubility in the electrolyte. 48 In the first case, lower ionic conductivity leads to compromised discharge capacities, while the latter results in a surface-mediated discharge product growth mechanism. Despite these research efforts, a practical and sustainable solution providing an optimal compromise between the viscosity, ionic conductivity, and stability of the electrolyte remains elusive. Consequently, it remains critical to obtain the necessary fundamental insights into the underlying interactions between the solvent and the discharge product(s) that can be used to identify the appropriate design rules to engineer optimal electrolyte environments. In the second case, when the discharge product-cathode interface plays the dominant role, gaining a fundamental understanding of the underlying interactions to tailor catalytically driven, surface-mediated mechanisms remains key. Successful implementation of this approach would decouple the role of the solvent and the electrode in Na-O<sub>2</sub> batteries. In such systems, solvents would primarily function as a transport media for M<sup>+</sup> cations, while the large compositional versatility of elements in the periodic table would be used to design an effective cathode electrocatalyst for selective growth of targeted and stable discharge products, such as NaO2. The realization of effective electro-

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To successfully develop a framework to identify the nature of the discharge product(s) and elucidate the atomic-scale interactions governing their growth, atomically controlled

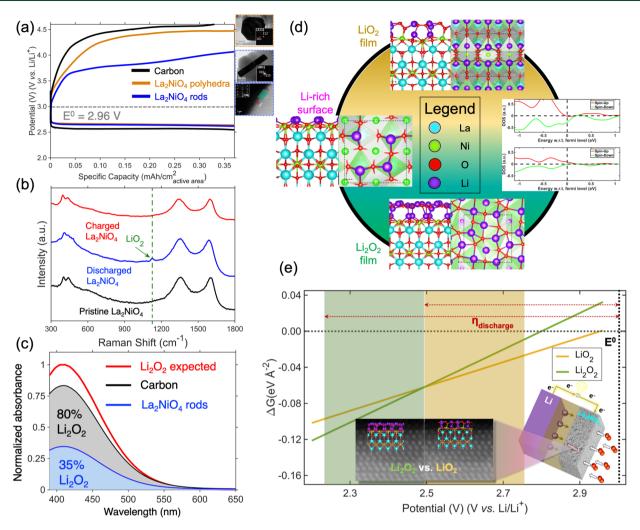


Figure 4. Combined experimental/theoretical framework for tuning catalysis at solid discharge product-electrode interface in Li-O<sub>2</sub> cathodes containing (001)-NiO-terminated rod-shaped La<sub>2</sub>NiO<sub>4</sub> oxide nanostructures. (a) Effect of the catalyst nanostructure (consequently surface structure) on the galvanostatic discharge-charge behavior at 37 µA cm<sup>-2</sup><sub>active area</sub> of a Li-O<sub>2</sub> battery (active area represents the Brunauer-Emmett-Teller (BET) surface area). The inset represents TEM and scanning transmission electron (STEM) micrographs of the nanostructured oxides (La<sub>2</sub>NiO<sub>4</sub>), highlighting their surface terminations. (b) Raman spectra of discharged and charged cathodes containing La2NiO4 nanorods, indicating reversible formation of LiO2 upon discharge. (c) Quantification of discharge products using hydrolysis-based titration on cathodes containing La<sub>2</sub>NiO<sub>4</sub> nanorods, suggesting a product distribution of 35% Li<sub>2</sub>O<sub>2</sub> and 65% LiO<sub>2</sub>. (d) Atomistic simulations of the interface between (001)-NiO-terminated La<sub>2</sub>NiO<sub>4</sub> and Li<sub>x</sub>O<sub>2</sub> species. (e) Potential-dependent phase diagram for the growth of LiO<sub>2</sub> and Li<sub>2</sub>O<sub>2</sub> on the surface of (001)-NiO-terminated La<sub>2</sub>NiO<sub>4</sub> surfaces during discharge, indicating stable formation of LiO<sub>2</sub> above discharge potentials of 2.5 V vs Li/Li<sup>+</sup>. The figure is reprinted from ref 20. Copyright 2019 American Chemical Society. Insets in (a) are reproduced with permission from refs 54 and 55. Copyright 2015 Royal Society of Chemistry and 2015 American Chemical Society, respectively.

syntheses of electrocatalysts with well-defined surface terminations, via approaches such as (i) single-crystal chemical deposition methods<sup>49,50</sup> or (ii) wet-chemistry-based synthetic methods (e.g., surfactant-mediated methods such as reserve microemulsion, hydrothermal methods, polyol-based approaches, or layer-by-layer deposition), are critical. 20,21,23,26,51-55 For example, the use of single-crystal electrodes has been key in elucidating the effects of the monometallic Pt cathode surface structure on the mechanisms associated with ORR and OER in Li-O<sub>2</sub> batteries. 49 However, with an increase in the complexity of the chemical composition of the cathode electrocatalyst beyond monometallic systems, synthetic control of the electrocatalyst surface structure becomes a challenge. A synthesis approach that has been successful toward addressing this challenge is reverse microemulsion, which has been shown to lead to control over the nanostructure of complex oxide electrocatalysts (i.e., La<sub>2</sub>NiO<sub>4</sub>

with a Ruddlesden-Popper (R-P) crystal structure) with welldefined oxide surface termination.<sup>20</sup> Such electrocatalysts have been reported to possess selective catalytic properties toward the growth of non-traditional, electronically conductive Lideficient discharge products ( $\text{Li}_x\text{O}_2$ ;  $1 \le x < 2$ ) in  $\text{Li}-\text{O}_2$ cathodes with electrolytes containing low DN (<20) solvents. 20,26,56-59 Figure 4a clearly shows that the electrocatalyst nanostructure, and consequently the underlying (001)-NiO surface facets of La2NiO4 nanorods, played a pivotal role in controlling the discharge product selectivity and the overall cell performance.  $^{20}$  Li-O $_2$  batteries containing (001)-NiOterminated La<sub>2</sub>NiO<sub>4</sub> nanorod electrocatalysts exhibited a ~0.7 V reduction in charge overpotentials, as compared to cathodes composed of only carbon or irregularly shaped La2NiO4 nanostructures. This reduction in the charge overpotential losses was ascribed to the changes that (001)-NiO-terminated La2NiO4 nanorods induced in the discharge product distribution (selectively catalyzing formation of  $\text{LiO}_2$  as opposed to  $\text{Li}_2\text{O}_2$ ). These insights were obtained by combining qualitative and quantitative characterization of the discharge products (LiO2 vs Li2O2) formed on these welldefined catalyst nanostructures using a combination of Raman spectroscopy (Figure 4b), hydrolysis-based titration (Figure 4c), and online electrochemical mass spectrometry. Similar methods can be directly extrapolated to Na-O2 systems. 14,36,40,60 In addition, controlled electrocatalyst synthesis coupled with detailed electrochemical and characterization studies was instrumental in providing the necessary link to atomistic simulations using periodic density functional theory (DFT) calculations to model the complex atomistic interactions governing discharge product growth on a catalyst surface.<sup>20</sup> Experimentally benchmarked theoretical models were used to demonstrate the formation of a conductive interface between the (001)-NiO-terminated La<sub>2</sub>NiO<sub>4</sub> surface and the formed  $\text{Li}_x O_2$  ( $0 \le x \le 2$ ) discharge product (Figure 4d,e), which would have been challenging to obtain via other means. A similar experimental/theoretical framework could be extrapolated to Na-O2 batteries for the advancement in understanding of the underlying chemistry at the solid discharge product—cathode interface. 17,18,20,22,26 Ultimately, an approach utilizing this framework would lead to identification of levers to control the charge overpotentials by tuning the energetics associated with discharge product oxidation at the solid discharge product-cathode electrocatalyst interface.

A key final step that needs be incorporated into this rigorous framework for surface-mediated discharge product growth mechanism is to determine the factors that could potentially lead to electrocatalyst deactivation over extended cycling. This is critical to ensure long-term stability of these batteries. Most studies generally ascribe loss in activity of an electrocatalyst to the accumulation of irreversible parasitic side products, such as carbonates. However, limited insights on the mechanism or properties of an electrocatalyst that lead to such deactivation or accumulation of parasitic irreversible products in non-aqueous aprotic alkali  $M\!-\!O_2$  batteries exist. Therefore, coupling the techniques described above with efforts to identify the factors that lead to electrocatalyst deactivation could result in a fundamentally new aspect of electrocatalyst design research for alkali  $M\!-\!O_2$  batteries.

In summary, studies related to Na-O<sub>2</sub> batteries have largely focused on solution-mediated discharge processes. With the ultimate goal of engineering stable Na-O2 batteries, we make the case for investigating surface-mediated mechanisms for these systems, such that the reversible formation of relevant products (NaO<sub>2</sub>) and their stabilization post discharge can be decoupled by minimizing solvent effects in these processes. As we discuss above, insights and approaches extrapolated from the Li-O2 electrochemistry can be used as stepping stones toward achieving this goal. Systematic fundamental studies, which consider the effects of the underlying electronic and geometric features of the electrocatalyst surface structure on the product distribution, are necessary to understand key features driving the surface-mediated discharge mechanism. Such studies would benefit from atomic-scale simulations, which can provide insights on key atomistic interactions at the solid-solid interface between the discharge product and the electrocatalyst surface. The complex nature of the underlying solid-solid interface between the discharge product and the electrocatalyst surface calls for rigorous benchmarking of Systematic fundamental studies, which consider the effects of the underlying electronic and geometric features of the electrocatalyst surface structure on the product distribution, are necessary to understand key features driving the surface-mediated discharge mechanism. Such studies would benefit from atomic-scale simulations, which can provide insights on key atomistic interactions at the solid—solid interface between the discharge product and the electrocatalyst surface.

theoretical calculations with experimental observations and will remain key to systematically guide the search for optimal electrocatalysts. In addition, effective stabilization of the desired discharge products in  ${\rm Na-O_2}$  batteries also requires an understanding of the factors that lead to the instability of the discharge products under different cell environments. Such an understanding, similar to the search for optimal electrocatalysts, can be gained by utilizing a synergistic approach involving controlled experimental and theoretical analyses to identify an effective strategy to minimize the instability of the discharge products in high DN solvents.

Finally, it is worth highlighting that the field of aprotic nonaqueous electrochemical systems, such as M-O2 batteries, can leverage insights from catalyst screening approaches routinely used in protic aqueous regenerative energy storage and conversion technologies, such as H<sub>2</sub> fuel cells. Specifically, the reaction chemistries pertaining to oxygen and hydrogen electrocatalysis (ORR, OER, hydrogen evolution and oxidation reaction (HER, HOR)) have largely benefited from systematic descriptor-based searches. These descriptor-based predictive tools utilize fundamental structure-property relationships,<sup>67</sup> such as linear scaling relationships and Sabatier volcano-type analysis, to identify promising new active, selective, and stable electrocatalysts. An extension of such descriptor-based analysis to non-aqueous systems, such as M-O<sub>2</sub> batteries, could be highly beneficial in the identification of active, selective, and stable electrocatalysts. This is especially important for M-O<sub>2</sub> chemistries, as (i) the opportunity for reducing the overpotential is much larger in these systems (~0.8 V of overpotential during charge in Li-O<sub>2</sub> systems) compared to aqueous protic systems (~0.3-0.4 V during ORR and OER) and (ii) selective production of the relevant discharge product remains key for the voltaic efficiency as well as the overall cyclability of the cell. However, realization of structure-property relationships presents a significant challenge in M-O<sub>2</sub> batteries due to the complex nature of the reaction chemistry and underlying atomic-scale structure. Nonetheless, methods and strategies are initially needed to decouple the roles of solvent, cathode, and potential in governing the underlying reaction mechanism. These insights can then aid in rational design of the underlying processes and guide the search toward more sustainable M-O<sub>2</sub> systems in a systematic manner compared to the currently adopted Edisonian approaches.

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### Notes

The authors declare no competing financial interest.

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