Rate-Dependent Nucleation and Growth of NaO$_2$ in Na-O$_2$ Batteries

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ABSTRACT: Understanding the oxygen reduction reaction kinetics in the presence of Na ions and the formation mechanism of discharge product(s) is key to enhancing Na–O2 battery performance. Here we show NaO2 as the only discharge product from Na–O2 cells with carbon nanotubes in 1,2-dimethoxyethane from X-ray diffraction and Raman spectroscopy. Sodium peroxide dihydrate was not detected in the discharged electrode with up to 6000 ppm of H2O added to the electrolyte, but it was detected with ambient air exposure. In addition, we show that the sizes and distributions of NaO2 can be highly dependent on the discharge rate, and we discuss the formation mechanisms responsible for this rate dependence. Micron-sized (~500 nm) and nanometer-scale (~50 nm) cubes were found on the top and bottom of a carbon nanotube (CNT) carpet electrode and along CNT sidewalls at 10 mA/g, while only micron-scale cubes (~2 μm) were found on the top and bottom of the CNT carpet at 1000 mA/g, respectively.

Rechargeable metal-air (oxygen) batteries are receiving intense interest as possible alternatives to lithium-ion batteries, in particular due to their potential to provide higher gravimetric energies.1–5 While much attention has been focused on aprotic Li–O2 batteries since their introduction in 1996 by Abraham et al.,6 substantial challenges must be addressed before widespread commercial exploitation is possible. These include the instability of aprotic electrolytes7 and oxygen electrodes,8,9 which contribute to low round-trip efficiency, poor rate capability, and poor cycle life. Recently, a metal-air battery in which lithium has been replaced by sodium has received increasing attention.10 Although Na–O2 batteries present lower gravimetric energies on a cell basis (1605 or 1108 Wh/kg based on Na2O2 or NaO2 discharge products, respectively)10 than Li–O2 batteries (3505 Wh/kg Na2O2),11 much lower charge overpotentials (~100 mV) than those in typical Li–O2 batteries (~1000 mV) have been reported12,13 based on reversible sodium superoxide (NaO2) formation (Na + O2 ↔ NaO2, E° = 2.27 V). Unlike Li–O2 batteries, for which Li2O2 is the only discharge product, Na2O214–15 sodium peroxide (Na2O2),16,17 and sodium peroxide dihydrate (Na2O2·2H2O)18,19 or a mixture,19–21 have been identified in Na–O2 batteries in ether-based electrolytes using a range of carbon electrode types. These products have been shown to have different morphologies: Na2O2 in micron-scale cubic shapes12,14 and nanorods22 Na2O2 in polycrystalline particles,16 and Na2O2·2H2O as rod-shaped particles or thin films.20 Unfortunately, the factors responsible for dissimilar discharge product chemistry and morphologies are still unclear, and no correlation has been found between the type of air electrode or electrolyte and the discharge product formed. Because the discharge product crystal structure, morphology (e.g., shape and thickness), and distribution are important parameters that influence the voltage profile on discharge and charge, the rate capability, the discharge capacity, and the reversibility in metal-air batteries,2,23 it is critical to gain insights into the oxygen reduction kinetics in the presence of Na ions and the nucleation and growth mechanisms of discharge products.

In this study, we investigate discharged Na–O2 cells with carbon nanotube (CNT) carpet cathodes to understand the effect of discharge kinetics on the formation of the discharge product. We analyzed the chemical composition of the discharge product using X-ray diffraction (XRD) and Raman spectroscopy and found that it consisted solely of NaO2. The formation of Na2O2·2H2O was not readily detected with the addition of water to the solvent (<6000 ppm); however, the evolution of Na2O2·2H2O was detected when we intentionally exposed the sample to the ambient environment. We also observed rate-dependent effects on the size and distribution of the discharge product. At high rates, micron-sized cubes were formed on the top and bottom interfaces between the CNT carpet and electrolyte, while at low rates, the entire thickness of the CNT carpet was more homogeneously covered with faceted nanoparticles. We show that this difference is consistent with
fast NaO$_2$ nucleation from solvated growth precursors at high rates, while at lower rates, diffusion of those precursors facilitates uniform growth of smaller nanoparticles.

We first examine the oxygen reduction reaction (ORR) kinetics of NaO$_2$ formation on CNT electrodes upon galvanostatic discharge. The CNT electrodes were carpets ($\sim$1 cm $\times$ $\sim$1 cm $\times$ $\sim$500 $\mu$m) of freestanding vertically aligned nanotubes with no binder. Figure 1a,b shows the voltage profiles at discharge rates of 10, 100, 250, 500, and 1000 mA g$^{-1}$ to a fixed capacity of 1000 mAh g$^{-1}$ and the discharge and charge curves of electrodes cycled at different rates to a fixed capacity (1000 mAh g$^{-1}$). A single flat discharge plateau is observed at all rates. At low current densities, a voltage plateau of 2.21 V corresponding to an overpotential of 60 mV is observed at all rates. At low current densities, a voltage plateau of 2.21 V corresponding to an overpotential of 60 mV is observed at all rates. At low (<0.01 mA cm$^{-2}$) and high current densities (>0.1 mA cm$^{-2}$) and high current densities (>0.1 mA cm$^{-2}$) and high current densities (>0.1 mA cm$^{-2}$) and high current densities (>0.1 mA cm$^{-2}$), however, the overpotential deviates from linear, Butler–Volmer-type behavior and decreases rapidly with increasing discharge current. It is interesting to note that Viswanathan et al.$^{26}$ developed a kinetic model for ORR in LiO$_2$ cells that led them to suggest that the curvature in the Tafel plot originates from a finite kinetic mismatch between reduction of adsorbed oxygen and adsorbed lithium-superoxide. They reported that this curvature is due to the contribution of superoxide disproportionation and irreversible side reactions to the measured electrode potential. A recent study by Bai et al.$^{28}$ has, however, shown that the kinetic behavior of carbon-coated LiFePO$_4$ electrodes, which also exhibit a nonconstant Tafel slope, closely matches predictions from Marcus–Hush–Chidsey theory, with the curvature controlled by the reorganization energy of reactant and product species involved in the electron transfer. The similarity between Tafel behavior in LiO$_2$ and NaO$_2$ batteries might therefore indicate a common rate-determining step (i.e., electron transfer to O$_2$ to form LiO$_2$ or NaO$_2$); however, further investigations of NaO$_2$ battery kinetic behavior are needed to better understand the deviations at low and high currents.

To probe the influence of soluble reaction intermediates on fundamental kinetic processes involved in NaO$_2$ electrochemistry, we performed cyclic voltammetry (CV) measurements of O/R/OER on a smooth glassy carbon disk surface in O$_2$-saturated 0.1 M NaClO$_4$ in DME using the rotating ring disk electrode (RRDE), with an Au ring used to oxidize soluble ORR products. Ring and disk current response curves in
Figures 1c,d, respectively, show that a greater number of soluble ORR intermediates are produced in Na⁺ than in the analogous Li⁺ electrolyte during the cathodic sweep when the ORR takes place. This difference was quantified in terms of the fraction of ORR charge (Q_{ORR}) composed of soluble (Q_{ring})/insoluble (Q_{ORR}) species as a function of rotation rate in Figure 1e,f and provides a basis for investigating how differences in Li−O₂ versus Na−O₂ discharge product distribution and morphologies can be explained using LiO₂ versus NaO₂ nucleation rates. These implications will be discussed in further detail later. During the anodic sweep, we observe an oxidation peak at 2.6 V versus Na⁺/Na on the ring, suggesting the participation of ORR charge (1000 mAh gc⁻¹) from NaO₂ 2H₂O upon exposure of NaO₂ to ambient air is supported and, accordingly, no such anodic peak is observed. This difference points to the presence of fundamentally different intermediate species during 2− versus 1-electron peroxide/superoxide oxidation processes, and whose precise identities future studies should investigate in greater detail using spectroscopic/structural methods.

Phase-pure NaO₂ (pyrite structure, Fm3m) was found as the only discharge product, confirmed by XRD and Raman spectroscopy. Figure 2a shows the XRD patterns for the CNT electrodes discharged at 10, 100, and 1000 mA gc⁻¹ to 1000 mAh gc⁻¹. Both diffraction peak positions and intensities agree well with NaO₂ (JCPDS reference card no. 01-077-0207). The other reflection maxima indicated in the diffractograms are related to the aluminum gastight sample holder. Moreover, Raman spectra support that NaO₂ is the main discharge product due to the presence of an intense peak at 1156 cm⁻¹ (Figure 2b), previously reported to be characteristic of this chemistry. It is important to note that carbonate species can be observed by Raman and have been observed upon discharge in alkyl carbonate-based electrolytes. We see no clear evidence of carbonate species, which is in agreement with recent differential electrochemical mass spectrometry (DEMS) analysis of Na−O₂ discharge, and suggests the formation of only trace amounts of carbonate side products upon discharge. The reversibility of the reaction on charge was also confirmed using XRD (Figure 2a), which shows that NaO₂ diffraction peaks completely disappear after charging.

We show, for the first time, that NaO₂ can be converted to Na₂O₂·2H₂O upon exposure to ambient atmosphere for short times (Figure 2c,d). While XRD revealed phase-pure NaO₂ for discharged electrodes in the sealed XRD holder after 1 h (Figure 2a), Na₂O₂·2H₂O (JCPDS 15-0064) was found to appear after longer scans of 2 and 3 h, which could be attributed to the reactivity of NaO₂ and water in ambient air associated with the leakage of the XRD holder. The fraction of the NaO₂·2H₂O phase increases after 3 h of exposure, becoming the dominant phase. The formation of Na₂O₂·2H₂O upon exposure of NaO₂ to ambient air is supported using Raman spectroscopy (Figure 2d), for which a characteristic peak for Na₂O₂·2H₂O appeared in addition to the NaO₂ peak (Figure S3 in the SI). The high reactivity of NaO₂ in air to form Na₂O₂·2H₂O may explain the appearance of these two discharge products in Na−O₂−cells reported in the literature if the discharge products were exposed to ambient air or considerable amounts of water. In this regard, several cells with electrolyte water content between 10 and 6000 ppm were examined upon galvanostatic discharge to observe the influence of water content on the discharge product (Figure S4 in the SI). Figure S4a shows the voltage profiles for cathodes discharged in electrolytes of various water contents at 100 mAh gc⁻¹ to a fixed capacity of 1000 mAh gc⁻¹ or 2000 mAh gc⁻¹ for the cell discharged with 6000 ppm of water. Phase-pure NaO₂ (pyrite structure, Fm3m) was found as the main discharge product, confirmed by Raman spectroscopy (Figure S4b in the SI) and XRD (Figure S4c) in all cells with up to 6000 ppm of water content in the electrolyte. Although the exact water content in the electrolyte could be influenced by reactivity with the Na negative electrode, increasing water content from 10 to 6000 ppm in the electrolyte led to changes in the NaO₂ morphology (Figure S5 in the SI), while no changes were found in the XRD data of the discharged product. This observation is in agreement with a recent study by Xia et al. reporting Na−O₂ discharge behavior in glyme-based electrolytes with up to 100 000 ppm of H₂O, where only NaO₂ was reported. These results therefore suggest that the conversion of Na₂O₂·2H₂O could not result from the reactivity between NaO₂ and H₂O alone, for which ~6400 ppm of water is required for direct conversion of all discharged NaO₂ to Na₂O₂·2H₂O. (See the SI for details of this calculation.)

The size and distribution of NaO₂ particles are a function of discharge rate. Figure 3a,b shows SEM images of the CNT electrode top surface (the O₂/electrode interface) at 10 and...
whereas at 1000 mA gc −1, small cubes and particles with sizes of ∼500 nm NaO2 cubes partially cover the surface (Figure 3a), whereas at high discharge rate (i.e., 1000 mA gc −1 or 0.1 μA cm−2) the NaO2 cubes were considerably bigger (∼2–10 μm) and cover the majority of the surface (Figure 3b). Figure 3c,d shows SEM images of interior cross sections of CNT carpets discharged at 10 and 1000 mA gc −1 to 1000 mAh gc −1. Upon discharge at 10 mA gc −1, we find sub-micron-scale cubes and small cubes and particles with sizes of ∼50 nm (Figure 3c), whereas at 1000 mA gc −1 the cross sections of the CNT carpets are mostly bare (Figure 3d). NaO2 cubes (∼400 nm at 10 mA gc −1 and 1.5 to 2.5 μm at 1000 mA gc −1) were also found at the separator/electrode interface (Figure 3e,f). Differences in sizes of sub-micron-scale cubes for the oxygen interface and cross-section at 10 mA gc−1 (Figure 3a,c) fell within the variation from region to region, while the sizes of cubes close to the separator interface were consistently smaller than those at the current collector interface (Figure 3e). Analysis of electrodes discharged at different gravimetric rates but the same capacity (Figure S6 in the SI) shows that the density of the nanometer-scale cubes and particles decreases with increasing discharge rate.

TEM imaging clearly shows nanometer-scale cubes and particles along CNT sidewalls in electrodes discharged at 10 mA gc −1 to 1000 mAh gc −1, where the top surface was covered with cubes characteristic of NaO2 crystals. Sub-micron-scale cubes partially cover the surface (Figure 3a), whereas at high discharge rate (i.e., 1000 mA gc −1 or 0.1 μA cm−2) the NaO2 cubes were considerably bigger (∼2–10 μm) and cover the majority of the surface (Figure 3b). Figure 3c,d shows SEM images of interior cross sections of CNT carpets discharged at 10 and 1000 mA gc −1 to 1000 mAh gc −1. Upon discharge at 10 mA gc −1, we find sub-micron-scale cubes and small cubes and particles with sizes of ∼50 nm (Figure 3c), whereas at 1000 mA gc −1, the cross sections of the CNT carpets are mostly bare (Figure 3d). NaO2 cubes (∼400 nm at 10 mA gc −1 and 1.5 to 2.5 μm at 1000 mA gc −1) were also found at the separator/electrode interface (Figure 3e,f). Differences in sizes of sub-micron-scale cubes for the oxygen interface and cross-section at 10 mA gc−1 (Figure 3a,c) fell within the variation from region to region, while the sizes of cubes close to the separator interface were consistently smaller than those at the current collector interface (Figure 3e). Analysis of electrodes discharged at different gravimetric rates but the same capacity (Figure S6 in the SI) shows that the density of the nanometer-scale cubes and particles decreases with increasing discharge rate.

TEM imaging clearly shows nanometer-scale cubes and particles along CNT sidewalls in electrodes discharged at 10 mA gc −1 (Figure 4a), in contrast with largely bare CNTs at 1000 mA gc −1 (Figure 4f). The nanoparticle sizes remained largely unchanged with increasing discharge capacity (Figure S7 in the SI). Energy-dispersive X-ray spectroscopy (EDS) (Figure 4c and 4h) revealed that after correcting for NaClO4 already in the electrolyte, these nanometer-scale particles like micron-scale cubes (Figure 4c,h) have a 1:2 ratio of Na to O, corresponding to NaO2 chemistry. Nanometer-scale NaO2 did not form along CNT sidewalls for electrodes discharged at 1000 mA gc −1, as evidenced by EDS (Figure 4h), which showed an elemental composition consistent with the NaClO4 salt, and electron diffraction (Figure 4j). The formation of these particles on CNTs was further supported by selected-area electron diffraction (SAED) patterns (Figure 4e and Table S1 in the SI), where all electron diffraction patterns could be indexed with the Fm3m structure of NaO2.

The precise growth mechanism responsible for the formation of micron-scale NaO2 cubes remains a matter of considerable debate. NaO2 cubes shown in Figure 3 are consistent with the theoretical Wulff shape reported by Lee et al. and the faceted shapes suggest a classical layer-by-layer growth mechanism, which has been proposed in pyrite FeS2 (pyrite). NaO2 cubes in this work also appear to display penetration twinning (Figure S9a in the SI), caused by the growth of misoriented crystals with common lattice points, and surface faceting (Figure S9b in the SI), both of which have been observed in FeS2. A fully analogous growth mechanism for NaO2 to pyrite growth, where O2 reduction to O2− is followed by stepwise Na+ addition on the solid NaO2 surface, is, however, unlikely given that (1) NaO2 has been widely assumed to be electrically insulating, which is supported by recent density functional theory (DFT) calculations, thus making direct O2 reduction on the NaO2 surface in layer-by-layer fashion difficult to envision and (2) ORR products have significant solubility in DME, which has been previously speculated and measured by RRDE here (Figure 1c,e) and in a recent study by Xia et al. NaO2 solubility in aprotic electrolytes raises the possibility that NaO2 cubes can grow via mesoscale self-assembly of solvated precursor species and high-order aggregates, similar to other electrically insulating metal oxide crystals, such as BaSO4, ZnO and CaCO3. It is worth noting that similar solution-mediated mechanisms have been proposed for Li2O2 growth in Li–O2 batteries.

Figure 3. SEM images of galvanostatically discharged CNT electrodes at (a,c,e) 10 mA gc−1 and (b,d,f) 1000 mA gc−1 to 1000 mAh gc−1, showing the O2/electrode (a,d) and separator/electrode (c,f) interfaces and cross sections of the CNT carpets (b,e), respectively.

Figure 4. TEM images of galvanostatically discharged CNT electrodes at (a,b,d) 10 mA gc−1 and (f,g) 1000 mA gc−1 to 1000 mAh gc−1. (b,g) Higher magnification images of regions in white boxes in panels a and f. (c,h) Energy-dispersive X-ray spectroscopy (EDS) spectrum from panels a and f. (e,j) Electron diffraction patterns from panels d and j, respectively.

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is essential to clarify details about this mechanism and is currently underway by the authors.

Large NaO₂ cubes found in regions of the carpet that have easy access to oxygen (O₂/electrode and electrode/separator interfaces) from high-rate discharge can be primarily explained by high NaO₂ formation rates. Indeed, previous studies have reported that the location of NaO₂ cubes in discharged carbon paper-based cathodes is highly dependent on the spatial variation of oxygen concentration in the cathode, such that a much higher concentration of cubes is found in regions/interfaces in direct contact with oxygen, than otherwise.²⁴,4² To investigate the hypothesis that the spatial variation in NaO₂ cube density at 1000 mA g⁻¹ could reflect a variation in local oxygen concentration across the CNT carpet, we modeled the steady-state distribution of oxygen in the electrolyte-filled pores across the electrode cross section by combining Fick’s diffusion law with electrochemical O₂ reduction parameters set by the applied current. (See the calculation in the SI.) The concentration of O₂ in the electrolyte-filled pores from the oxygen-rich interfaces toward the interior of the electrode is shown in Figure S10 in the SI. At low rates (10–100 mA g⁻¹), there is a negligible drop in the O₂ concentration across the electrode thickness. This is consistent with the ORR and thus solid NaO₂ formation occurring uniformly throughout the CNT carpet. In contrast, at 1000 mA g⁻¹, a ~60% drop in the O₂ concentration across the electrode is expected. This result is, however, at odds with TEM images of electrodes discharged at 1000 mA g⁻¹ (Figure 4f), where there is negligible discharge product in the electrode interior. It is additionally inconsistent with what we observe in CNT cathodes discharged at a comparable rate of 1000 mA g⁻¹ in 0.1 M LiClO₄ in DME, where no Li₂O₂ toroids are observed,²⁴,4³ and the discharge product is typically more uniformly distributed (Figure S11 in the SI), although similar steady-state oxygen concentrations would be expected in that electrolyte. Thus, using the steady-state O₂ concentration model, the moderate concentration gradient of molecular oxygen found in the electrolyte at high rates such as 1000 mA/g (SI) is not sufficient to explain the formation of large NaO₂ crystals on the top and bottom of the CNT carpet but not within it.

A more likely hypothesis is one in which the NaO₂ particle size and distribution is dictated by the concentration of reduced O₂⁻−Na⁺ species in the electrolyte and the nucleation and diffusion of (O₂⁻−Na⁺)ₙ aggregates of different sizes formed in the electrolyte during discharge (Figure S12 in the SI). We estimate that the discharge capacity that can be achieved with O₂ dissolved in the interior of the CNT carpet alone is ~20 mAh/g, which is ~2% of the total discharge capacity (SI). At high rates, these oxygen molecules can be reduced to O₂−−Na⁺ species, which could nucleate on the CNT surface to form a coating of solid NaO₂ (2% capacity). Upon continued discharge at high rates, dissolved oxygen molecules in the electrolyte above and beneath the CNT carpet could be reduced to soluble O₂−−Na⁺ by the current collector and Na negative electrode, respectively. Given the high discharge rate, the concentration of these soluble O₂−−Na⁺ species can quickly build up above and beneath the CNT carpet (Figure S12 in the SI, B1), which can lead to the formation of large (O₂−−Na⁺)ₙ aggregates in solution (Figure S12 in the SI, B2). These aggregates are expected to have much lower diffusivity than molecular O₂ and O₂−−Na⁺ species and will cluster at the top and bottom of the interfaces of the CNT carpet, where large NaO₂ cubes then grow (Figure S12 in the SI, B3). At low rates, oxygen molecules initially dissolved in the electrolyte are reduced to O₂⁻−Na⁺ species; however, given the low discharge rate, reduced O₂−−Na⁺ species form above and beneath the CNT carpet at a slow rate and can diffuse throughout the carpet without quickly aggregating. This results in a more uniform concentration of O₂⁻−Na⁺ across the carpet (Figure S12 in the SI, C1) and the formation of smaller (O₂−−Na⁺)ₙ aggregates in solution (Figure S12 in the SI, C2) than those formed at high rates. Soluble O₂−−Na⁺ species and small (O₂−−Na⁺)ₙ aggregates are expected to have greater diffusivity than large (O₂−−Na⁺)ₙ aggregates in the electrolyte within the CNT carpet, which results in a more uniform distribution of NaO₂ cubes within the carpet (Figure S12 in the SI, C3). In contrast, during Li₂O₂ formation at similar rates, we observe slower nucleation kinetics to allow the diffusion of reduced oxygen species throughout the whole carpet, thus facilitating more uniform growth.²⁵

We support this hypothesis by estimating the difference in thermodynamic barriers to NaO₂ versus Li₂O₂ nucleation from classical nucleation theory, which holds that the thermodynamic barrier for nucleation of a crystal phase ΔGₐ depends on its surface energy γ and the degree of supersaturation of reactants σ⁴⁴,⁴⁵

\[
\Delta G_{\text{C}} \propto \frac{\gamma^3}{(RT \ln \sigma)^{3/2}}
\]

γ represents the average surface energy of the crystal, normalized by the area fraction of each exposed facet: γ = Σ γᵢ × Aᵢ, where γᵢ is the surface energy of a particular facet and Aᵢ is its surface area fraction. Using first-principles DFT calculations, Kang et al.⁴⁶ have recently estimated a surface energy for the low index (100) terminations of cubic NaO₂ (Pa₃) of 11.7 meV/Å², resulting in an γ of 11.7 meV/Å². Mo et al.⁴⁷ use a similar approximation to DFT as in ref 46 to compute a hexagonal Wulff construction for Li₂O₂ that is dominated by the (0001) and (1120) facets with surface energies of 25 and 34 meV/Å², respectively, under oxidizing conditions. Assuming a crystal of unit volume with a 64% area fraction composed of the oxygen-rich basal (0001) terminations (0001) terminations⁴⁸ and 36% (1120) results in a γ of 28.2 meV/Å², which is ~2.5 times as high as that of NaO₂. Because ΔGₐ is a cubic function of γ, this suggests a nucleation barrier for NaO₂ that is ~14 times lower than Li₂O₂.

Supersaturation σ is defined as

\[
\frac{[a_{\text{M}⁺}]^y[a_{\text{O}₂⁻}]^z}{K_{\text{sp}}}
\]

where we take [a_M⁺] and [a_O₂⁻] to be the solution activities of the alkali metal (M = Na⁺ or Li⁺) and O₂⁻ ions, respectively, where y is 1 or 2 for NaO₂ and Li₂O₂, respectively, and Kₛ₉ is the solubility product of bulk phase NaO₂ or Li₂O₂. To our knowledge, standard Kₛ₉ values of Na₂O₂ and Li₂O₂ in DME are not known. For this calculation, we assume that the bulk solid is in equilibrium with its solvated constituent ions such that

\[
\mu_{\text{Na}⁺}^\circ + \mu_{\text{O}₂⁻}^\circ - \mu_{\text{NaO}₂}^\circ = -RT \ln K_{\text{sp}}
\]

\[
2\mu_{\text{Li}⁺}^\circ + \mu_{\text{O}₂⁻}^\circ - \mu_{\text{Li}_2\text{O}_2}^\circ = -RT \ln K_{\text{sp}}
\]

where μ⁺ is the standard state ion formation energy and μ is the chemical potential of the solid. μ for NaO₂ and Li₂O₂ is calculated from their standard values, while μNa⁺ and μLi⁺ are inferred from regression analysis performed by Gritzner."
relating half-wave redox potentials of metal cations to the donor number of the solvent used. Using superoxide and peroxide ion formation energies from redox potentials reported by Sawyer and Gibian, the LiO2 solubility product is \( \log_{10} K_\text{sp}^{\text{LiO}_2} = -21.7 \), while \( \log_{10} K_\text{sp}^{\text{NaO}_2} = -18.4 \). We approximate activities of soluble ionic species as concentrations. As Li2O2 and Na2O2 crystal precursor concentrations in the CNT carpet cannot be directly measured during the ORR, we propose that differences in the solubility of superoxide-related species in 0.1 M NaClO4 versus 0.1 M LiClO4 in DME reflect this difference. From RRDE measurements during the ORR in O2-saturated 0.1 M NaClO4 in DME, we estimate the fraction of \( Q_\text{ORR} \) charge that is composed of these species to be 60% (Figure 1e), which is in good agreement with the analogous RRDE ring-disk current ratio in 0.1 M NaOTf in DME recently reported by Xia et al. In contrast, this ratio is ~20% for ORR in Li+ (Figure 1f). Assumming these solubilities reflect a difference in the actual concentration of soluble O2- species during discharge enables us to approximate superoxide supersaturation during NaO2 than Li2O2 growth on the basis of a 10 mM15 oxygen concentration. This results in supersaturations of \( 4.6 \times 10^{26} \) and \( 1.6 \times 10^{25} \) for Li2O2 and Na2O2 respectively. Combining this result with the cubic scaling relationship between \( \Delta G_f \) and \( \gamma \) yields a nucleation barrier that is ~12 times smaller for Na2O2 than Li2O2 formation and is consistent with the conclusion that Na2O2 nucleation is much faster than Li2O2, particularly because the nucleation rate is exponentially dependent on the thermodynamic nucleation barrier. We note that although this analysis does not include quantitative changes to this barrier as a function of discharge overpotential, recent work by Kang et al. suggests that increasing the discharge overpotential decreases nucleation barrier even further from its value at the equilibrium potential. This trend is in agreement with our hypothesis that Na2O2 nucleation is faster at higher rates. We also note that changes to crystal surface energies as a result of solvent molecule adsorption and kinetic barriers to precursor formation such as ion desolvation are not taken in account. Nevertheless, given the ability for such thermodynamic analysis to predict phase selection in several natural/geological mineral systems such as CaCO3 and more relevantly, in Na–O2 batteries, we believe a significant difference in NaO2 versus Li2O2 nucleation barriers is expected and reflects an important first-order difference in the relevant physical parameters dictating relative rates of their bulk phase nucleation. In support of the lower diffusivity of \( \text{O}_2^- - \text{Na}^+ \), aggregates compared with oxygen, we note that the effective hydrodynamic radius of O2 in DME is 0.12 nm, \( r \), while the size of the critical nucleus of NaO2 at 1 atm has been calculated at ~1 nm for discharge potentials <2.0 V versus Na+/Na. Assuming \( \text{O}_2^- - \text{Na}^+ \), aggregates nucleated in solution are of roughly the size of critical NaO2 radii and that their diffusivity as well as that of O2 follows the Stokes–Einstein relation (where diffusivity is inversely proportional to hydrodynamic radius), the diffusivity of the aggregates will be expected to be ~10 times less than that of molecular O2.

In summary, the sole discharge product after Na–O2 cell discharge is sodium superoxide (NaO2), as indicated by XRD and Raman spectroscopy. NaO2 can convert to Na2O2·2H2O upon exposure to ambient atmosphere, but Na2O2·2H2O cannot be formed in Na–O2 cells, even when 6000 ppm of H2O is added to the electrolyte. Discharge at low rates results in micron-scale and nanometer-scale NaO2 cubes on the top and bottom of CNT carpets and along the CNTs in the interior of the carpet, while at high rates, micron-scale NaO2 cubes form only on the top and bottom surfaces of CNT carpets and no nanoscale NaO2 particles are detected along CNT sidewalls in the interior of the carpets. We explain this difference on the basis of high local supersaturation and thus fast nucleation of \( \text{O}_2^- - \text{Na}^+ \), aggregates with low mobility at the oxygenated top and bottom interfaces of the CNT carpet at high rates but lower supersaturation, slower nucleation of \( \text{O}_2^- - \text{Na}^+ \), aggregates, greater diffusion throughout the CNT carpet, and thus more uniform growth, at lower rates. We justify the importance of the competition between NaO2 crystal nucleation kinetics and precursor diffusion by showing that the estimated thermodynamic barrier for NaO2 nucleation is 12 times lower than that for Li2O2, implying faster NaO2 growth kinetics. This is consistent with the rate dependence of the spatial distribution of NaO2 previously outlined and more uniform discharge product formation for Li2O2 growth at both low and high discharge rates. The insights obtained from integrating electrochemical, structural, chemical, and kinetic components involved in Na–O2 battery discharge could enable new strategies for maximizing energy density of practical Na–O2 electrodes.

**EXPERIMENTAL METHODS**

**Cyclic Voltammetry Measurements.** Three-electrode cells consisted of a 5 mm diameter GC disk as the working electrode (5 mm diameter), an Au ring electrode (6.5 mm inner diameter, 7.5 mm outer diameter), and a sodium or lithium foil counter and reference electrode. RRDE experiments were performed in a water-free argon glovebox (H2O < 0.1 ppm, O2 < 1%). 0.1 M LiClO4 in DME was purchased from BASF, USA and used as received, while 0.1 M NaClO4 in DME was prepared. NaClO4 salt was purchased from Sigma-Aldrich and vacuum-dried at 150 °C for 24 h prior to electrolyte mixing. RRDE measurements were performed in O2-saturated electrolyte by sweeping the disk between 1.8 and 4.0 V versus Na+/Na, while the ring is held at 3.0 V versus Na+/Na to oxidize soluble O2- species converted to it from the disk under rotation up to 1600 rpm. In the analogous Li–O2 case, the disk was swept between 2.0 and 4.5 V versus Li+/Li, while the ring is held at 3.5 V versus Li+/Li. We assume the ring oxidation charge reflects the detection of solution-based O2- species produced during ORR and estimate the fraction of \( Q_\text{ORR} \) charge that is composed of these species by normalizing it to the theoretical collection efficiency, \( \eta \), of the RRDE geometry: \( Q_\text{agg}/\eta Q_\text{ORR} \), where in our case, \( \eta \) is 23.5%. \( \eta \) was calibrated using the reversible O2/O2- couple in dimethyl sulfoxide; however, the collection efficiency using the well-known ferrocene/ferrocenium (Fc/Fc+) couple yielded a similar value of 25.8%. The other component of \( Q_\text{ORR} \) thus reflects surface-bound or insoluble species, represented by \( Q_\text{agg}/\eta Q_\text{ORR} \).

**Cell Assembly and Electrochemical Measurements.** The fabricated Na–O2 cells consisted of a sodium metal anode and freestanding vertically aligned few-walled CNT carpets (detailed preparation of the nanotubes has been previously reported) as the O2 electrode (~1 x 1 cm). The electrodes were vacuum-dried at 100 °C for 8 h and transferred to a glovebox (H2O < 0.1 ppm, O2 < 0.1 ppm, Mbraun, USA) without exposure to the ambient environment. Carbon loading of ~1 mg/cm2 was used. Ethylene glycol dimethyl ether, (C2H4O2, DME), (anhydrous, 99.5% Sigma-Aldrich) was used as the electrolyte solvent and sodium perchlorate (NaClO4, 98%, Sigma-Aldrich) as the conducting salt. DME and sodium perchlorate.
perchlorate were dried over molecular sieves (3 Å) for 1 week and under vacuum at 150 °C for 24 h, respectively. The electrolyte solution of 0.1 M NaClO₄ in DME was prepared in a glovebox with a final water content of <10 ppm, determined by C20 Karl Fisher coulometer (Mettler Toledo). Cells were assembled with sodium metal (Sigma-Aldrich, 15 mm in diameter) and two Celgard C480 separators (Celgard, USA, 18 mm diameter) were soaked in 120 μL of electrolyte. A stainless-steel mesh was used as the current collector. Following assembly, cells were transferred to another connected argon glovebox (Mbraun, USA, H₂O < 1 ppm) and were sealed with a rubber O-ring, in order to minimize exposure to atmospheric contaminants before and during XRD measurements. glovebox and sealed in an airtight XRD sample holder (Anton Paar, Graz, Austria), facilitating an X-ray transparent plastic dome, sealed with a rubber O-ring, in order to minimize exposure to atmospheric contaminants before and during XRD measurements.

Raman Spectroscopy Measurements. Raman spectroscopy was conducted on the discharged electrodes in a LabRAM HR800 microscope (Horiba Jobin Yvon) using an external 20 mW He:Ne 523 nm laser (Horiba, Jobin Yvon), focused with a 50X long working distance objective. A silicon wafer was used for calibration.

SEM Characterization. SEM images were taken using a Zeiss Supra55VP and Ultra55 (Carl Zeiss AG, Germany). Images were taken with an in-lens detector at 5 kV operating voltage. Samples were sealed and stored in argon before being rapidly moved into the SEM chamber to minimize air exposure.

TEM Characterization. High-voltage TEM studies were performed at 200 kV on a FEI Tecnai (G2 Spirit TWIN) multipurpose TEM.

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**ASSOCIATED CONTENT**

* Supporting Information Additional characterization data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.5b00919.

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