The Nature and Impact of Side Reactions in Glyme-based Sodium–Oxygen Batteries

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Although Na–O₂ batteries have a low overpotential and good capacity retention, degradation reactions of glyme-based electrolytes are the primary reason for inefficiency in cell performance. The discharge capacity is accounted for through analysis of the side-products. Although sodium superoxide is the primary product (90% theoretical), quantitative and qualitative evaluation of the side-products (using ¹H NMR, isometric titration, and on-line mass spectrometry) shows the presence of sodium acetate (~3.5%), and three-fold less sodium formate, methoxy (oxo)acetic anhydride, and sodium carbonate. Our reaction mechanism proposes two paths for their formation. Because the side-products are not fully removed during oxidation, they accumulate on the cathode during cycling. Resting the cell at open circuit potential during discharge results in consumption of the superoxide through the reaction with diglyme, which greatly increases the fraction of side products, as also confirmed by ex situ reaction studies. These findings have implications in the search for more stable electrolytes.

Introduction

Aprotic alkali metal–O₂ batteries have been the focus of much attention. Li–oxygen batteries were the first to garner interest owing to their high theoretical gravimetric energy density (3505 Wh kg⁻¹ with respect to the mass of Li₂O₂), based on a two-electron reduction process (Li⁺ + O₂ + 2 e⁻ → Li₂O₂) at a potential of 2.96 V, and low mass reactants (Li metal and gaseous O₂). This combination makes the Li–O₂ battery a very appealing system for applications in which high gravimetric energy is important, such as electric vehicles. Achieving a practical battery, however, has proven difficult owing to numerous drawbacks, including electrochemical performance: low rate capability,[1–3] poor cycle life,[7,8] and a high charge overpotential.[5,6] More recently, a seminal report on Na–O₂ batteries[9] has triggered intensive follow-up studies. Its performance is superior to that of the Li–O₂ battery with respect to charge overpotential (~0.1 V vs. 1 V), rate capability, and cycling retention.[10] In aprotic media, the Na–O₂ cell typically forms solid sodium superoxide during discharge—not sodium peroxide—through a one electron process (Na⁺ + O₂ + e⁻ → NaO₂) at a potential of E° = 2.27 V vs. Na/Na⁺.[10] Although the theoretical energy density of the Na–O₂ battery (~1100 Wh kg⁻¹) is much lower than that of the Li–O₂ battery, its good performance has been suggested to provide the foundation of a more practical cell.[12] We have shown that its electrochemistry relies on a proton phase transfer catalyst (PPTC) that facilitates the formation and oxidation of NaO₂ in solution via the HO₂ intermediate.[13] The proton can be, and is in practice, derived from any source such as impure salt hydrates, the inclusion of trace moisture from the system, or weak acids owing to their reaction to produce the highly soluble HO₂ radical.[14] The low charge overpotential allows the battery to operate within an electrochemical window that minimizes oxidation side-products during charge.[11] Thus, the superior reversibility of the Na–O₂ battery is thought to be because of the “cleaner” chemistry associated with the oxygen reduction/evolution (ORR/OER) reactions, at least in the first cycle.[15] Nonetheless, given the high reactivity of superoxide (NaO₂) and the strongly nucleophilic nature of the O₂⁻ ion and the HO₂ radical, electrolyte degradation is expected.

To date, Na–O₂ cells have employed glyme-based electrolytes; typically, diethylene glycol dimethyl ether (diglyme). Glymes have been the mainstay electrolytes for many Li–O₂ batteries owing to their quasi-stability to superoxide attack, although mass spectrometry,[16,17] NMR,[18] and X-ray photoelectron spectroscopy (XPS)[19] studies have shown that they react to produce a variety of Li–carboxylate decomposition products. These block catalytic surfaces ites for oxidation, inhibit cycling. It is possible to mitigate glyme degradation through protection of the backbone that inhibits hydrogen abstraction,[21] but the resulting electrolyte is highly viscous owing to the formation of a solvent–ion pair. Dimethyl sulfoxide has been reported to be a more suitable electrolyte in Li–O₂ batteries in conjunction with a gold cathode,[22] but its reactivity is observed in the presence of carbon cathodes.[23,24] Cells using N,N-dimethylacetamide coupled with LiNO₃ to stabilize the...
negative electrode surface have been shown to cycle effectively, although reactivity is still an issue. To date, no electrolyte has been reported that is inert in the aprotic metal–oxygen cell and also possesses excellent electrolyte properties. The carbon cathode is also susceptible to oxidation in a Li–O₂ battery, especially during charge. Attempts have been made, with some success, to alleviate cathode decomposition through the use of alternative non-carbon or passivated carbon cathodes. The low mass of carbon and its high surface area are still unmatched with respect to overall gravimetric energy density and cost.

Here, we explore the chemistry of Na–O₂ batteries in diglyme electrolytes. Following from the work first reported by McCloskey et al., we define the origin and precise nature of the side products in the cell, quantify and propose a mechanism for their formation, and address some potential drawbacks of this system. The Na–O₂ battery benefits from a very low overpotential during charge owing to the solubility of NaO₂/H₂O₂, which facilitates its oxidation and thus exhibits ostensibly better cycling performance than Li–O₂ cells that lack a redox mediator. Nonetheless, analysis shows that formation of decomposition products during discharge—which are largely not removed during charge—are more problematic than previously thought. These side-products are the origin of the rise in potential near the end of charge. Furthermore, resting the cell at open circuit potential in the presence of NaO₂ results in dramatic consumption of the superoxide through reaction with diglyme. Very significant fractions of carboxylate side products are formed. Evidence shows that the main source of degradation stems from the strong nucleophilic character of the discharge product, NaO₂, as well as the reactivity of the O₂⁻/H₂O₂ radical.

**Experimental Section**

**Cathode preparation.** Stainless steel meshes with an area of 0.78 cm² (100 x 100 mesh) were sonicated in ethanol and dried prior to use. A slurry of ground ¹³C carbon (Sigma–Aldrich) and polytetrafluoroethylene (PTFE) (from a 20 mg/500 mL isopropanol stock solution) was prepared in a 85:15 mass ratio. After it was mixed for 1 min, the slurry was pressed onto the stainless steel mesh and dried in air at 60 °C for 1 h. The cathodes were dried at 300 °C under vacuum overnight in a Büchi oven and transferred to an Ar-filled glovebox.

**Electrochemical measurements.** Cathodes were employed in either 2 or 3-electrode-modified polyfluoroalkoxy polymer (PFA) Swagelok cells. Each cathode was placed in a cell with a sodium metal (Sigma–Aldrich) anode, separated by two glass fiber separators and one celgard separator (2500). Electrolyte (240 µL) composed of 0.5 M sodium trifluoromethanesulfonate (NaOTf; prepared in-house) and 15 ppm H₂O in distilled diethylene glycol dimethyl ether (DEGDME, or diglyme) was added to the cell. The cell was then sealed and pressurized to 1.5 atm in 5.0 research grade oxygen (Praxair). Prior to measurement, the cell pressure was monitored with a pressure transducer (PX409, Omega) to ensure that each cell was hermetically sealed. The electrochemical measurements were performed with an Arbin galvanostat/potentiostat.

The current density for all experiments was 130 µA cm⁻²; capacity and voltage limitations are as indicated.

**Determination of NaO₂ content.** Iodometric titration of the dry cathode contents was performed using a slightly modified version of a previously reported method, see the Supporting Information for details.

**¹H NMR.** NMR experiments were conducted in D₂O on a 300 MHz Bruker Advance spectrometer at room temperature. ¹H NMR spectra were referenced to the residual HOD peak at 4.78 ppm. The fraction of decomposition products was determined through integration of the peak area with respect to a known amount of benzenzene standard added to the solution. This stock solution was prepared using 100 g of D₂O and 0.2 mL benzene and was allowed to equilibrate for 24 h prior to analysis. Cathodes and separators were removed from the cell with washed with tetrahydrofuran (THF) The contents were then left to dry under vacuum for 12 h and backfilled with argon before addition of the D₂O/benzene solution. 0.8 mL of the stock solution was added to the cell contents and collected for measurement.

**KO₃ reaction.** KO₃ (Sigma–Aldrich) and 18-crown ether (Sigma–Aldrich) were used as received. Diglyme was distilled prior to use and NaOTf was prepared as indicated above. For each reaction, 0.02 g KO₃ and 0.13 g dicyclohexyl-18-crown-6 (crown ether) were added to 2.5 mL diglyme. The reaction was left to stir for four days. To produce NaO₂, 0.10 g NaOTf was added immediately following the addition of KO₃ and crown ether. The added NaOTf was twice the molar amount of KO₃ to ensure complete reaction of the O₂⁻ to NaO₂. After four days, the solid contents were left to settle and were collected using a centrifuge. The contents were washed three times with 15 mL THF and dried under argon overnight. D₂O was added directly to the solid contents for NMR analysis.

**Mass spectrometry (electrochemistry).** To measure gas evolution during cell charge, the cathodes were first discharged using the same Swagelok design described above. Upon completion of the discharge, the cell contents (without the metallic sodium electrode) were immediately transferred to an El-Cell electrochemical cell in an argon-filled glove box and an additional 50 µL of electrolyte was added. The cells were attached in-line with an RGA 200 (Stanford Research Systems), and a continuous flow of 5.0 argon (Praxair) was used to sweep the evolved gases during cell charge across a 50 µm diameter capillary. Quantification was performed using a calibration curve composed of different concentrations of O₂/CO₂ in Ar (0–2000 ppm).

**Mass spectrometry (chemical).** The method for chemical analysis of carboxylates/carbonates was adapted from Thotyl et al. Cells were discharged/charged to specific capacities and removed after immediately upon completion after a specific rest period as indicated in the text. Both the cathode and separator were removed and placed into a custom-design glass reaction vessel. This vessel was fitted with Swagelok microconnects for ease of connection inline with the mass spectrometer. The vessel was sealed air-tight with a fitted septum. The cell was left to rest under flowing argon for 1 h prior to measurements. The Ar flow rate was then set to 1 mL min⁻¹, and approximately 0.5 mL of 2 M H₃PO₄ were added to the cell contents and stirred. The evolved gases were swept into the mass spectrometer, and the reaction was left to continue until CO₂ levels returned to base level. The concentration of CO₂ (and ¹³CO₂) was measured and quantified using the same method as for
the electrochemical mass spectrometry experiments mentioned above.

**Scanning electron microscopy.** Cathodes were removed from cells immediately after completion of discharge or charge (no rest unless indicated). The cathodes were washed with THF, dried under vacuum, and mounted onto SEM stubs with double sided carbon tape in a hermetically sealed argon-filled box. Transfer from the glovebox to the SEM was performed with minimal (∼1 s) exposure to the atmosphere upon placement into the SEM load-lock chamber. Analysis was performed with a Zeiss Ultraplus FESEM.

**X-ray diffraction.** XRD measurements were performed using a Bruker D-8 Advance diffractometer employing CuKα radiation (λ = 1.5406 Å). Samples were mounted on a silicon low-background holder using a moisture-protective barrier.

**XPS.** XPS measurements were performed on electrodes that were removed immediately upon completion of a discharge/charge cycle, with prior washing with THF to remove the electrolyte/salt. The electrodes were dried and transferred under argon to the XPS instrument. The binding energy values were calibrated to the adventitious carbon C 1s peak at 284.8 eV.

### Results and Discussion

In our study, 13C-labelled cathodes were used to identify the source of decomposition reactions in the Na–O2 cell by tracing their origin to either the reaction of the carbon surface or of the 13C-glyme-based electrolyte. To determine the nature of the discharge products, a cell was discharged and charged to a capacity of 1 mAh in 0.5 m NaOTf/diglyme. The electrolyte consisted of distilled diglyme, with pure, crystalline NaOTf (synthesized in-house to ensure no contamination from NaOH·H2O or other species) and 15 ppm H2O to provide a controlled, albeit very low, fraction of the phase-transfer catalyst necessary to achieve good discharge/charge properties, as previously reported. Figure 1a shows an electrochemical profile for a cell first discharged to 1 mAh, and charged to an upper cutoff voltage of 4.5 V, along with the associated gas evolution quantified by on-line electrochemical mass spectrometry (OEEMS). The discharge potential of 2.1 V and initial charge plateau at 2.3 V is representative of a typical Na–O2 cell, and in agreement with most other reports that utilize carbon-based cathodes and exhibit NaO2 as the discharge product.[10,11,15] The presence of crystalline Na2O2 as the single discharge product is confirmed by its diffraction pattern (Figure S1). We note that a few reports have documented the formation of Na2O or Na2O2 hydrate, as the discharge product with similar carbon cathodes and glyme-based electrolytes.[33-36] Although the parameters that determine the selectivity of products are not well understood, we observe some Na2O2 hydrate on long exposure of the cell to rest periods, as discussed in the next section. Such cells exhibit poor rechargeability and much larger overpotentials compared to Na2O, similar to Li2O2.[33,34] The formation energies of bulk Na2O2 and Na2O2 are quite close and slightly favor the formation of Na2O2, but the lower surface energy of nanocrystals that are initially nucleated thermodynamically favors the production of Na2O.[12] The phase transfer catalyst kinetically drives the growth of this phase upon initial nucleation of the superoxide, as previously demonstrated.[13]

The electrochemical charge plateau at 2.3 V in Figure 1a is accompanied by a flat oxygen evolution profile measured by OEEMS that corresponds to the near theoretical 62.0 nmol min⁻¹ O2 evolution (based on a 100 μA discharge current). The voltage rises to 3.0 V as oxygen evolution declines to zero, suggestive of an overpotential that must be exceeded to complete the process, and which we ascribe to an impedance layer (see below). Integration of the amount of O2 evolved (28.6 ± 0.1 μmol) with respect to the total charge passed up to 3.0 V corresponds to 1.10 e⁻/O2, as expected, based on the one-step oxidation of Na2O to Na⁺ and O2 (Figure 1b). Deviation from the theoretical 1.00 e⁻/O2 ratio agrees closely with other reports.[13,15] The loss in charge efficiency results from electrochemical side reactions that produce degradation products (see below), in addition to a very small fraction of NaO2 entrapment in the separator owing to its dissolution in the electrolyte, as has been mentioned by others.[15] After the initial charging step, a subsequent stepped voltage profile from 3.0 V to 4.5 V is characterized by CO2 evolution starting at approximately 3.2 V followed by a trace of additional O2 evolution above 3.8 V. CO2 evolution is ascribed to the oxidation of sodium carboxylates present on the cathode surface, similar to that exhibited by Li–O2 cells.[17] The gas evolution of both CO2 and O2 both ceases before electrochemical electrolyte oxidation is signalled by the onset of a flat voltage profile at 4.45 V. The amount of Na2O2 on cathodes discharged to 1 mAh was determined to be 33.9 ± 0.5 μmol by iodometric titration,
In parallel, similarly prepared electrodes were present in the cell. The amount of NaO$_2$ that remained on the cathode surface after charging the cell to 3.0 V was also measured by iodometric titration. That voltage corresponds to the end of the initial O$_2$ evolution profile, but before CO$_2$ evolution starts. At 3.0 V, 1.8 µmol of NaO$_2$ still remained, equivalent to about 5% of the NaO$_2$ that was deposited during discharge. This explains the lower-than-ideal capacity measured during charge to this point (−0.85 mAh vs. 1 mAh). The capacity on charge can be fully accounted for based on the amount of NaO$_2$ on discharge (90% of theoretical), less the NaO$_2$ that remains at 3.0 V (5%). The second oxygen evolution process in Figure 1a between 3.8 and 4.4 V corresponds to oxidation of the remaining NaO$_2$, as determined by iodometric analysis of the product at 4.4 V. Only a trace (−0.4 µmol of NaO$_2$) remains after this point, indicating that virtually all of the NaO$_2$ is removed prior to the start of electrolyte oxidation at 4.5 V.

**Identity of discharge products and their quantification**

To assess and quantify the carboxylate and carbonate products formed during discharge, the $^{13}$C positive electrode and separators were washed in THF and dried under vacuum. They were subjected to acid treatment with 2 M H$_2$PO$_4$ utilizing online mass spectrometry to quantify the total evolved CO$_2$ ($^{13}$CO$_2$) gases.$^{[15]}$ In parallel, similarly prepared electrodes were immersed in D$_2$O to extract the soluble species, providing the $^1$H NMR spectrum shown in Figure 2. The relative contribution of carboxylate side-products was estimated from peak integration. Experiments were performed in duplicate, and the amount of the side-products was determined from the combined analysis. A majority of the degradation product is composed of sodium acetate (−4% of total discharge product), along with equal contributions of sodium formate, methoxy(oxo)acetic anhydride, and Na$_2$CO$_3$ (−1% each of the total discharge product). These data are summarized in Table S1 and Figure 3, which express the products as a percentage of the total theoretical NaO$_2$ expected. Only a miniscule fraction of the total decomposition products (−0.5%) originate from the carbon cathode as Na$_3^{13}$CO$_3$. To confirm that the addition of D$_2$O or H$_2$PO$_4$ does not promote the formation of these products, XPS analysis was performed on a freshly discharged cathode without any treatment other than a THF wash. C 1s signals corresponding to C–O–Li (formate/acetaldehyde) and C–O (formate/acetate/carbonate) unequivocally confirm the degradation products are produced from the chemical reactions taking place during cell operation (Figure S2). The O 1s spectrum also shows the existence of NaO$_2$ as a major product, together with a small fraction of carboxylate degradation products (Figure S3). A more detailed discussion of the XPS analysis is available in the Supporting Information.

The amount of carboxylate degradation products formed during discharge depends on the cathode composition. Comparison of a very low surface area carbon fiber cathode (Freudenberg GDL, H2315), with a high surface area carbon (Vulcan$^{[16]}$) (Table S2) shows that the Freudenberg cathode exhibits a much higher fraction of NaO$_2$ formed as a function of current passed (98%). This is reflected in the low fraction of decomposition products, which are also less than those observed from the $^{13}$C cathode. In contrast, the NaO$_2$ and carboxylate fraction exhibited on the Vulcan$^{[16]}$ electrode is similar to that of the $^{13}$C electrode. These findings agree with a study by Bender et al., which reports dramatic differences in the electrochemical performance of different carbon cathodes in the Na–O$_2$ cell.$^{[18]}$ They report that the discharge capacity as well as charge efficiency is de-
Determined on the cathode material, with charge efficiencies ranging between 75–93%. The wide range is most likely owing to variability in the decomposition products, although their nature was not addressed in that study. A comprehensive examination of the role of the carbon is also beyond the scope of the present work. For our study, 13C cathodes were used to distinguish degradation products from the electrolyte from those arising from the carbon cathode.

Because NaO2 is charged at a relatively low potential (owing to phase transfer catalysis) Na–O2 chemistry is reported to be less affected by side-reactions[11,15] in the Li–O2 system, decomposition products are formed during discharge, but a significant fraction are also produced during the oxidation step owing to the high overpotential required to oxidize Li2O2.[15, 16, 17, 32] Furthermore, as shown by Thiøyl et al.[26] the stability of the carbon cathode is also an issue: above 3.5 V the carbon undergoes oxidation in the presence of Li2O2 to form Li2CO3. To confirm that the decomposition products are formed mostly during discharge in the Na–O2 cell, the products analyzed above were compared to those remaining after a cell was charged to 3.0 V after prior discharge to 1 mAh (Table S1). Analysis was again performed by a combination of 1H NMR to determine carboxylate contributions and acid treatment/mass spectrometry (see Figure S4). In agreement with McCloskey et al.,[13] the fraction of decomposition products produced during charge is minimal, as summarized in Figure 3. The relative ratio of formate, acetate, carbonate, and anhydride is very similar to that of the discharged cathode, implying that there is no additional decomposition during charge. The only difference is the amount of Na213CO3, which increases by approximately three fold compared to that of the discharged cathodes. Thus, although the charge overpotential for the NaO2 cell is very low (~0.1 V vs. theoretical), the voltage is sufficient to promote slight oxidation of the cathode, forming a very small fraction of Na213CO3 by the direct oxidation of carbon with NaO2:

\[
5 \text{NaO}_2 + 2^{13}\text{C} \rightarrow 2\text{Na}_3^{13}\text{CO}_3 + 2\text{O}_2 + \text{Na}^+ + e^- 
\]

To determine if all or any of these carboxylate decomposition products are removed at elevated voltage and correspond to the CO2 evolution that is centered at approximately 3.5 V, the products were analyzed using the method described above, after the cell was charged to 4.4 V. These results are also summarized in Figure 3. We found that the amount of all the carboxylate products decreases after charge to 4.4 V, but they are still present. XPS of the charged electrodes (Figure S2 and S3) corroborates this conclusion. It suggests that only a fraction can be oxidized, consistent with the small amount of CO2 that is evolved. In a recent study we probed the electrochemical oxidation of Li-based decomposition products. We demonstrated they could not be oxidized on a carbon surface at a potential below the stability window of the glyme-based electrolyte, without a catalyst.[39] The inability to oxidize carboxylate decomposition products on a carbon surface in Li–O2 cells at a low potential (~4.7 V vs. Li/Li+) was also reported by Gasteiger et al.[46] and Leskes et al.[14] Therefore, either the 4.4 V charge voltage in the Na–O2 cell is below the necessary potential to oxidize the carboxylate side-products, or they are continuously formed in tiny amounts during the charge process.[40, 39] The former is more likely. We further conclude that NaO2 can be oxidized in the presence of indelible, insoluble electrolyte decomposition products because solution-based proton phase transfer catalysis (PPTC) governs the charge process.[13] The oxidation of Li2O2 does not pass via an LiO2 intermediate,[41] and hence a proton phase transfer catalyst in the Li–O2 battery has little positive effect during charge.[42] The large overpotential during oxidation of Li2O2 is also partly owing to the presence of surface carboxylates, which increase the surface impedance.[43] The oxidation of NaO2 in solution mediated by PPTC is not impeded by the presence of these degradation products, however, leading to a lower charge overpotential.

Decomposition mechanisms

Hydrogen abstraction from glyme by the highly nucleophilic O2− species is a known cause of dimethoxymethane decomposition in Li–O2 cells, which leads to the formation of lithium formate and lithium carbonate on the cathode surface.[15, 44] Recent work also suggests that the reactivity of Li2O2 with water used to determine speciation in NMR experiments may exacerbate carboxylate formation.[46] Much research has been dedicated to the mitigation of electrolyte degradation by exploring alternative solvents, such as sulfones,[47] amides,[48] ionic liquids,[49] and backbone-protected ethers,[51] but no truly stable electrolyte has been discovered yet. In Li–O2 cells another source of reactivity is the surface of the discharge Li2O2 product. Significantly, using a combination of computational techniques, Kumar et al. showed that the rate of glyme decomposition is faster on the superoxide-terminated (O22−) surface of Li2O2 than on its peroxide-terminated (O22−) surface.[50] It was proposed that the highly reactive superoxide surface of Li2O2 accelerates the degradation of glyme by a very similar mechanism to that of hydrogen abstraction by O2−. This has implications for the Na–O2 cell, as it implies that the superoxide Na2O2 surface will play a major role in the production of these decomposition products, as we confirm below.

The sodium formate, sodium acetate, and methoxyl(oxo)acetec anhydride products identified in the cell using NMR analysis enable us to propose a mechanism for the decomposition of diglyme and higher order glymes (see Figure 4). In this scheme, sodium formate is generated via Path 1, whereby a methyl hydrogen (H+) abstraction by O2− is followed by β-scission of an ether bond to give formaldehyde, which is then oxidized by highly nucleophilic NaO2 to formate. The mechanism by which sodium acetate is generated requires translocation of a hydrogen atom to generate the required methyl-containing two carbon unit of acetate. The most plausible mechanism by which this could occur is an intramolecular 1,5-hydrogen abstraction, which conforms to the reactivity profile expected for radical species. A dialkyl ether radical (such as that generated during the initial β-scission of Path 1) would be expected to undergo a 1,5-hydrogen abstraction to give a ther-
Effect of side-products on cycling and stability at open circuit potential

The fact that NaO₂ and carboxylate products are not completely removed during charge to a typical 3.0 V has implications for cell cycling. Figure 5a shows a typical electrochemical curve of a cell cycled four times with a charge voltage limitation of 3.0 V, followed by a 4.4 V cutoff at the end of the 5th charge. Figure 5b shows SEM images of the cathode surface at the end of the 5th discharge. The surface is covered with 8 μm NaO₂ cubes that possess a relatively clean and smooth surface. Figure 5c shows the cathode surface at the end of the 5th charge, at a potential limit of 3.0 V (chosen to correspond to the initial O₂ evolution peak in Figure 1a). Here, the surface is not covered with pristine NaO₂ cubes, but is populated with smaller structures. These resemble collapsed cubes that appear to have been oxidized from the center outwards to leave behind a roughened shell. This suggests that the inner NaO₂ product is oxidized from within the interior of the cubes (through proton phase transfer catalysis in solution, leaving the surface of the cubes covered with sodium carboxylate products, which require a high overpotential for stripping. On cycling, these products accumulate along with the NaO₂. This was confirmed by iodometric titrations: 4.48 μmol of NaO₂ remain after 5 cycles at a charge cutoff of 3.0 V, which is greater than the amount of NaO₂ remaining after a single discharge/charge cycle (1.80 μmol).

To completely remove the remaining decomposition species, the cathode was charged on the 5th cycle to 4.4 V; beyond the point of CO₂ and O₂ gas evolution, but below that
of electrolyte decomposition. The SEM image in Figure 5d shows a relatively clean surface. Unsurprisingly, the amount of CO$_2$ and O$_2$ that is evolved during the 5th charge process beyond 3.0 V is greater than that of charging beyond 3.0 V for a single cycle (Figure S5). In summary, although the generation and decomposition of NaO$_2$ could occur during cycling in a narrow window if it were the only product, charge to higher voltage is necessary to completely remove the remaining NaO$_2$ that is trapped as a result of the accumulation of carboxylate-based decomposition products. However, this is not a suitable method to improve Na–O$_2$ cell cycling.

The effect of cycling a cell to an upper potential limit of 4.4 V is illustrated by the working electrode profile (Figure 6a). On subsequent discharge, an overpotential that precedes the normal ORR discharge plateau is ascribed to the reduction of a species generated at a high charge potential, although its nature has not yet been identified. In contrast to Hartmann et al., the cell can still discharge after it is charged to a high potential. Another difficulty with a high voltage charge cutoff is illustrated in Figure 6b, which shows a plot of the potential of the working potential of the anode with respect to a sodium metal reference electrode. Charging a Na–O$_2$ cell to the voltage necessary to remove carboxylates is clearly detrimental to the anode. The overpotential required to strip sodium increases with each subsequent cycle, implying the growth of insulating layers that form on the metallic sodium anode. We speculate that this results from the accumulation of decomposition products and impedance layers that form on the metallic sodium anode. This is in contrast to a cell operated within the potential window between 1.8 V vs. 3.0 V, where the stripping/plating profile of the anode does not change upon cycling and the stripping voltage is much lower, as shown in Figure 5d. Such a profile is similar to electrochemical stripping/plating of lithium in glyme-based electrolytes. However, the cell is only able to achieve <20 cycles with an upper voltage cutoff of 3.0 V (Figure S7), before capacity fading begins, followed by eventual cell termination. Visual inspection of the cathode (inset, Figure S7) suggests that accumulation of the discharge product on the cathode surface is the cause of cell termination. In short, other methods are necessary to completely charge the NaO$_2$ and remove the decomposition products, as their removal through electrochemical charge not only requires a high overpotential, but also accelerates decomposition on the anode of the Na–O$_2$ battery.

Reactivity of superoxide/sodium superoxide at open circuit potential

Reactivity of NaO$_2$ with diglyme can be of concern for the lifetime of Na–O$_2$ cells that utilize this electrolyte (which at the time of this publication, are the majority of reports), as any period of rest in a cell at open circuit voltage (OCV) could induce electrolyte decomposition and consumption of the superoxide. To “mimic” OCV conditions following discharge, diglyme was reacted with KO$_2$ in the presence of crown ether. Superoxide, i.e., “solvated O$_{2^-}$” is liberated through chelation of K$^+$ ions with dicyclohexyl-18-crown-6 (crown ether). This method was previously utilized to determine electrolyte stability. For comparison, a second solution was prepared with the same concentration of KO$_2$/crown ether, except NaOTf was added to the reaction after 1 h of reaction to immediately trigger precipitation of NaO$_2$. Reactivity of the solvated O$_{2^-}$ can thus be partly distinguished from that of solid NaO$_2$, although we recognize that sodium superoxide itself has some—albeit limited—solubility in diglyme. After the solutions were allowed to stir to mimic cell conditions, the solids were recovered and analyzed using $^1$H NMR. Regardless of whether solvated O$_{2^-}$ or NaO$_2$ is present, formate and acetate were both observed; however, 3–5 fold more of these products was generated if formation of NaO$_2$ is triggered (Figure S8). Furthermore, the ratio of formate/acetate varies. In the presence of O$_{2^-}$, sodium formate is the most abundant decomposition product and only a minimal amount of sodium acetate is observed (sodium acetate/sodium formate = 0.18). In the presence of NaO$_2$, the proportion of sodium acetate is three times greater (sodium acetate/sodium formate = 0.60). Although we do not yet fully understand the reason for the difference, it may result from the difference between solution versus surface reactivity.

The reactivity of NaO$_2$ within the cell was further confirmed by discharging the cathodes to a capacity of 1 mAh and holding the cell at an open circuit for a period of 100 h. SEM images that compare a freshly discharged cathode surface (Figure 7a) to a discharged cathode held for 100 h (Figure 7b) show that the NaO$_2$ cubic morphology is greatly altered after extended diglyme exposure. A similar phenomena was observed by Hartmann et al. in accord, the amount of NaO$_2$ determined by iodimetric titration is drastically reduced. Only 16 μmol of NaO$_2$ remains, which amounts to 43% of the theo-

![Figure 6. a) Working electrode and b) counter electrode potential of a Na–O$_2$ cell using a $^{13}$C cathode cycled 5 times with an upper potential limit of 4.4 V. Plating of sodium onto the anode occurs when the cathode is charged, and stripping of the anode occurs when the cathode is discharged.](image-url)
retical value, and nearly 50% less than that of the Na₂O content of a freshly discharged cathode (Figure 7c). X-ray diffraction analysis of the cathode, shown in Figure 7d, reveals that some of the Na₂O converts to Na₂O₂·8H₂O, which is expected to require a high voltage to oxidize. Compared to the freshly discharged cathode, the reduction in fraction of superoxide is also associated with a very large increase in the amount of carboxylate-based decomposition products (Figure 7e). Although the fraction of sodium carbonate doubles during the rest period, the fraction of sodium acetate increases by as much as 50-fold, with a much lower increase in sodium formate. It is clear that the reaction pathway of sodium acetate formation (Figure 4 above) is kinetically favored compared to the formation of sodium formate. We postulate that, after the initial scission, the fragmented anion radical remains on the Na₂O₂ surface (to produce sodium acetate), while the formaldehyde dissolves in solution and thus its conversion to sodium formate is less favored, by comparison. This agrees with the quantification of the reaction products described above, which shows an increased fraction of sodium acetate resulting from contact of diglyme with Na₂O. The SEM images (Figure 7a,b) indicate that the interior of the Na₂O₂ cubes have been etched away in this process, leaving hollow outer shells. It suggests that the outer surface of the Na₂O₂ crystallites react with diglyme to form an incomplete passivating layer of side-products, and as the cubes crack, dissolution/reaction of the interior superoxide follows.

Conclusions

Our study of the decomposition products formed during operation of a Na–O₂ battery shows that during cell discharge, solvated O₂⁻ and Na₂O react with both the carbon cathode and the diglyme electrolyte to form a variety of Na-carboxylate decomposition products. Little additional decomposition occurs during charge. The consumption of Na₂O through chemical reaction with diglyme (to form sodium carboxylates) gives rise to the majority of the capacity loss. Even in the presence of these decomposition products, a large overpotential is not observed for the oxidation of Na₂O (in contrast to Li–O₂ batteries) owing to the dominance of a solution-based process mediated by a phase transfer catalyst. However, since the decomposition products cannot be oxidized within the narrow electrochemical window that ideally characterizes the Na–O₂ cell, they accumulate over many cycles, leading to cell death. This is different from the Li–O₂ cell, where electrolyte degradation is exacerbated during charge owing to inherently high overpotentials unless redox mediators are invoked. In the Li–O₂ cell, the rapid conversion of transient lithium superoxide to lithium peroxide means that superoxide does not aggravate glyme degradation during discharge. Thus, although the low charge overpotential of the Na–O₂ cell does limit the amount of decomposition products that form during charge, the highly reactive O₂⁻ (or HO₂⁻), as well as the nucleophilic character of the Na₂O itself, make (poly)glyme-based electrolyte degradation in the Na₂O₂ cell a very real concern. This is especially true during storage unless the cell is fully charged, because the formation of Na₂O₂·8H₂O occurs upon extended exposure, which would require a high voltage to oxidize. The performance of the Na–O₂ cell is nonetheless very promising because of its low overpotential, and once significant improvements in electrolyte stability are achieved, very good cycling properties and charge efficiency can be expected.

Keywords: batteries · degradation · electrochemistry · electrolytes · sodium–oxygen

cell, it cannot explain the lower than expected 8768 – 8772.

[50] S. Meini, N. Tsiouvaras, K. Schwenke, M. Piana, H. Bever, L. Lange, H. A. Gasteiger, J. Phys. Chem. Lett. 2015, 6, 9795 – 9799. We note that although analogous reactivity cannot be completely discounted in the Na – O cell, it cannot explain the lower than expected NaO (90%) fraction in the cell, and the fact that our analysis accounts for most of the side-products observed.


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