

Competitive Oxygen Reduction Pathways to Superoxide and Peroxide during Sodium-Oxygen Battery Discharge

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The sodium-air battery offers a sustainable, high-energy alternative to lithium-ion batteries. Discharge in the cell containing glyme-based electrolytes can lead to formation of large cubic NaO₂ particles via a solution-precipitation mechanism. While promising, high rates result in sudden death. The exact nature of the discharge product has been a matter of contention, and Na₂O₂ has never been directly detected in a dry glyme Na–O₂ cell. If Na₂O₂ were to form during discharge in the Na–O₂ cell it

would have a detrimental impact on cell performance. Here we show that Na₂O₂ forms during discharge at high overpotential in the glyme-based Na–O₂ batteries. Na₂O₂ formation is confirmed by spectroscopic and electrochemical analysis and electron microscopy demonstrates that it results in thin insulating films at the electrode surface. The formation of these thin films results in rapid cell death during discharge, introducing an inherent chemical limitation to the Na–O₂ battery.

Introduction

Metal-air (O₂) batteries are promising high specific energy alternatives to lithium-ion batteries.^[1–11] In the aprotic sodium-oxygen (Na–O₂) battery, sodium metal is oxidized on discharge and oxygen is reduced at the positive electrode.^[12–14] In Na–O₂ batteries containing glyme-based electrolytes, NaO₂ is found to

be the major discharge product and it is commonly reported to form large cubic crystals.^[12,15–17] The formation of NaO₂ crystals occurs via the dissolution of NaO₂ at the electrode surface and its subsequent precipitation away from the electrode. The solubility is controlled in part by the solvent donor number, as is the case in the Li–O₂ system,^[18–20] as well as the Na⁺ activity.^[21] Several publications have shown promising results with this system.^[4,13,22–24] Advantages of the Na–O₂ battery compared to the Li–O₂ battery stem from the formation of a superoxide rather than a peroxide, as this simple electrochemical reaction and soluble product results in relatively low polarisation and higher rates during cycling.^[2,7,25,26] However, parasitic chemical reactions can occur, impacting on the cyclability of cells. This arises from reactions of both the Na electrode and the NaO₂ discharge product, but careful selection of electrolytes and cycling parameters can mitigate these issues.^[27,28]

At high rates, the capacity of typical glyme-based Na–O₂ cells is lower and sudden death of the cell is common.^[2,29,30] This has been linked to the formation of NaO₂ thin films at the electrode surface.^[20,29] We have shown that this is in part due to the limited solubility and rate of (de)solvation of NaO₂,^[31] which must be rapid enough to sustain the dissolution-precipitation mechanism by which NaO₂ cubes grow.^[20,29] However, computational studies have shown that electrochemical formation of Na₂O₂ may also be possible at higher overpotentials.^[15] It is well known that in the Li–O₂ cell, O₂ is reduced to Li₂O₂, which is more stable than LiO₂.^[19,32–35] Unlike the Li–O₂ system, the theoretical equilibrium potentials for the formation of NaO₂ and Na₂O₂ from oxygen are only 60 mV apart (2.27 V for NaO₂ and 2.33 V for Na₂O₂ vs. Na/Na⁺). If Na₂O₂ were to form during discharge in the Na–O₂ cell it would have a detrimental impact on cell performance and remove many of its advantages over the Li–O₂ battery. The discharge product(s) and performance of Na–O₂ cells are influenced by several factors, including electro-

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lyte composition and the nature of the electrode surface.^[12,31,36] Na_2O_2 has been observed in the cell with acetonitrile and NaO_2 has been shown to disproportionate to Na_2O_2 in this solvent.^[37] This is ascribed to the low donor number of acetonitrile. Attempts have been made to form Na_2O_2 in other electrolytes, but these require conditions which enhance the surface binding of NaO_2 , such as the use of Au electrodes, in conjunction with high overpotentials.^[38] Some Pt facets and Cu nanoparticles have also been shown to favour Na_2O_2 formation on discharge.^[39,40] Na_2O_2 has been observed when discharging at high overpotential at a TEM grid, noting that this contains both carbon and gold.^[41] Hydrated peroxide ($\text{Na}_2\text{O}_2 \cdot \text{H}_2\text{O}$) and NaOH have been reported in glyme-based electrolytes due to contamination of the system with water from sources including the O_2 gas supply and electrolyte.^[14,42] Although, trace quantities of water have also been shown to promote NaO_2 solution growth via phase-transfer catalysis.^[43] During standard cycling conditions (dry electrolyte with a carbon electrode), it is generally assumed that Na_2O_2 does not form during discharge in the $\text{Na}-\text{O}_2$ cell containing glyme ethers.

Here we explore the impact of overpotential on the electrochemical reduction of oxygen in the glyme-based $\text{Na}-\text{O}_2$ batteries and the role this plays in product selection, NaO_2 versus Na_2O_2 , and cell performance. The capacity is measured

at various rates and as is the distribution, morphology, and chemistry of the discharged product at the positive electrode. Electrochemical analysis is used to propose discharge routes that explain these observations. The formation of thin Na_2O_2 films is conclusively demonstrated and shown to be detrimental to cell performance.

Results and Discussion

Impact of discharge rate on the capacity of the sodium- O_2 battery

To explore the impact of discharge rate, and thus overpotential, on the discharge product and capacity of the $\text{Na}-\text{O}_2$ battery, a series of Swagelok-type $\text{Na}-\text{O}_2$ cells were discharged at three different current densities: 0.025, 0.25 and 0.4 mA cm^{-2} . The electrolyte was 0.5 M sodium triflate (NaOTf) in diethylene glycol dimethyl ether (DEGDME) and the electrode was carbon, consistent with state-of-the-art cells.^[31] Figure 1(a) shows the discharge profiles collected from the $\text{Na}-\text{O}_2$ cells. At a lower current density of 0.025 mA cm^{-2} , the battery achieved a relatively large discharge capacity of over 4 mAh cm^{-2} , which is typical for an $\text{Na}-\text{O}_2$ cell. The dominant formation of NaO_2 is

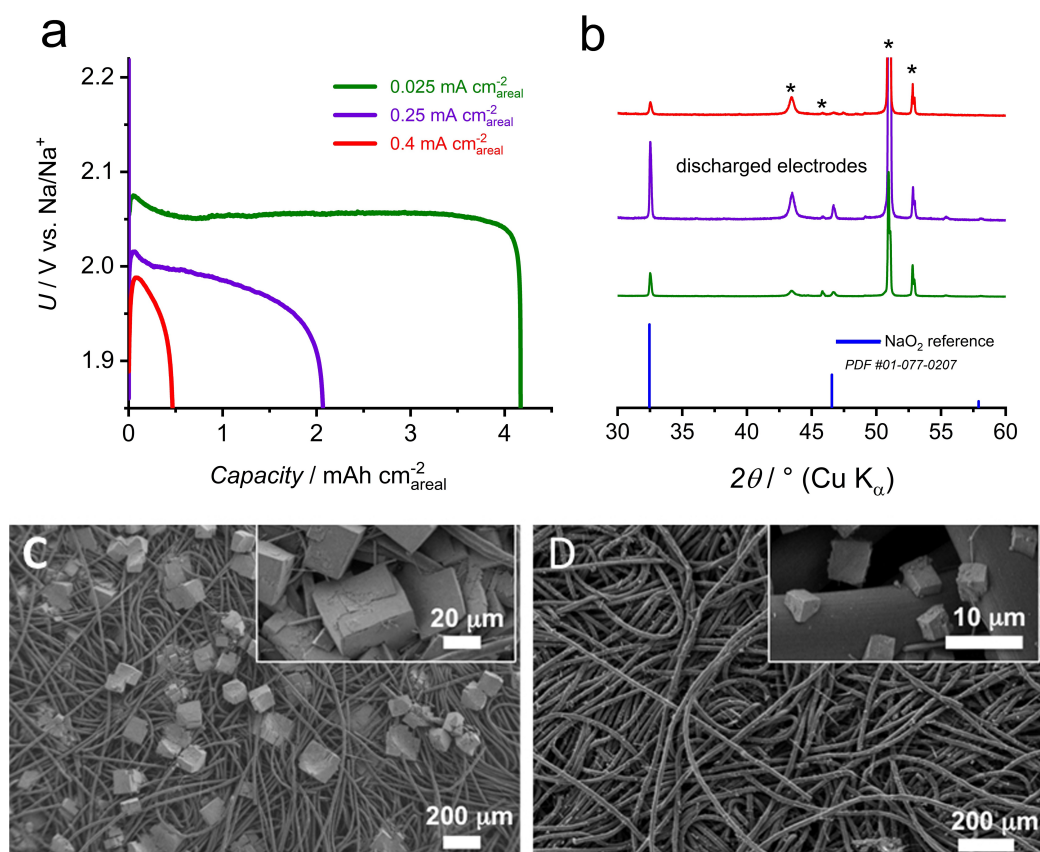


Figure 1. Discharge performance of $\text{Na}-\text{O}_2$ (Swagelok) cells: a) discharge profiles at three different current densities using O_2 saturated 0.5 M NaOTf in DEGDME; b) the corresponding PXR D patterns of the discharge positive electrodes. Three current densities are used: 0.025 mA cm^{-2} (green line), 0.25 mA cm^{-2} (purple line) and 0.4 mA cm^{-2} (red line). Peaks marked with a black asterisk (*) correspond to the sample holder and GDL. SEM images of the positive electrode after discharge at c) 0.025 mA cm^{-2} and d) 0.4 mA cm^{-2} .

confirmed by powder X-ray diffraction (PXRD), Figure 1(b). Figure 1(c) shows an SEM image of the discharged positive electrode showing numerous large cube-shaped structures, consistent with the dominant formation of NaO_2 by a solution precipitation mechanism.^[2,13,20] Upon increasing the current density to move to practical values, the voltage of the discharge plateaus shifted negative, discharge capacities decreased dramatically, and the cell death (rapid negative shift in voltage) rapidly occurred, Figure 1(a). This is also accompanied by an initial drop in potential, which we suggest is associated with the nucleation barrier for formation of NaO_2 on the carbon surface, Figure S1. SEM images, Figure 1(d), showed that the NaO_2 cubes became smaller and fewer in number at a higher current density. Previous studies have shown that current density has an impact on NaO_2 particle size.^[20,31,44] PXRD indicates that the only product is NaO_2 , Figure 1(b). Interestingly, cubic NaO_2 does not completely cover the electrode surface and large areas of apparent bare carbon remain. Passivation of the electrode surface by NaO_2 cubes at high rates cannot explain cell death.

Soluble versus surface-grown discharge products

To investigate the electrochemistry of oxygen reduction in Na^+ -ion-containing DEGDM in more detail, we employed a rotating ring-disk electrode (RRDE), Figure 2. Oxygen is reduced at the

rotating disk electrode (i_{disk}), while any soluble O_2^- formed is detected at a ring electrode (i_{ring}) by holding it at an oxidising potential (3.7 V vs. Na/Na^+). The difference between the ring and the disk current can be assigned to insoluble products (i_{surface}), e.g., $\text{NaO}_{2(s)}$, $\text{Na}_2\text{O}_{2(s)}$ and can be used to identify the electrochemical potential at which a second reduction reaction occurs. NaO_2 does not disproportionate to form Na_2O_2 in Na^+ -ion containing DEGDM and therefore only electrochemical routes need to be considered.^[37] The disk current rapidly increases between 2.5 V and 2.0 V vs. Na/Na^+ . At low overpotentials, i_{disk} mirrors i_{ring} , indicating that the reaction is almost exclusively forming dissolved O_2^- , rather than solid NaO_2 . At higher overpotentials, i_{ring} no longer fully accounts for i_{disk} and this coincides with a peak in the current followed by a drop to zero current, demonstrating passivation of the electrode surface by the discharge product. The potential at which this occurs mirrors the sudden death potential of the $\text{Na}-\text{O}_2$ cells and indicates that it is responsible for the limited capacity seen at high overpotentials.

Surface confined discharge products in the sodium- O_2 battery

To identify the nature of the passivating film, $\text{Na}-\text{O}_2$ cells were constructed using carbon nanofiber as the electrode (prepared as described in the Supporting Information), which are suitable

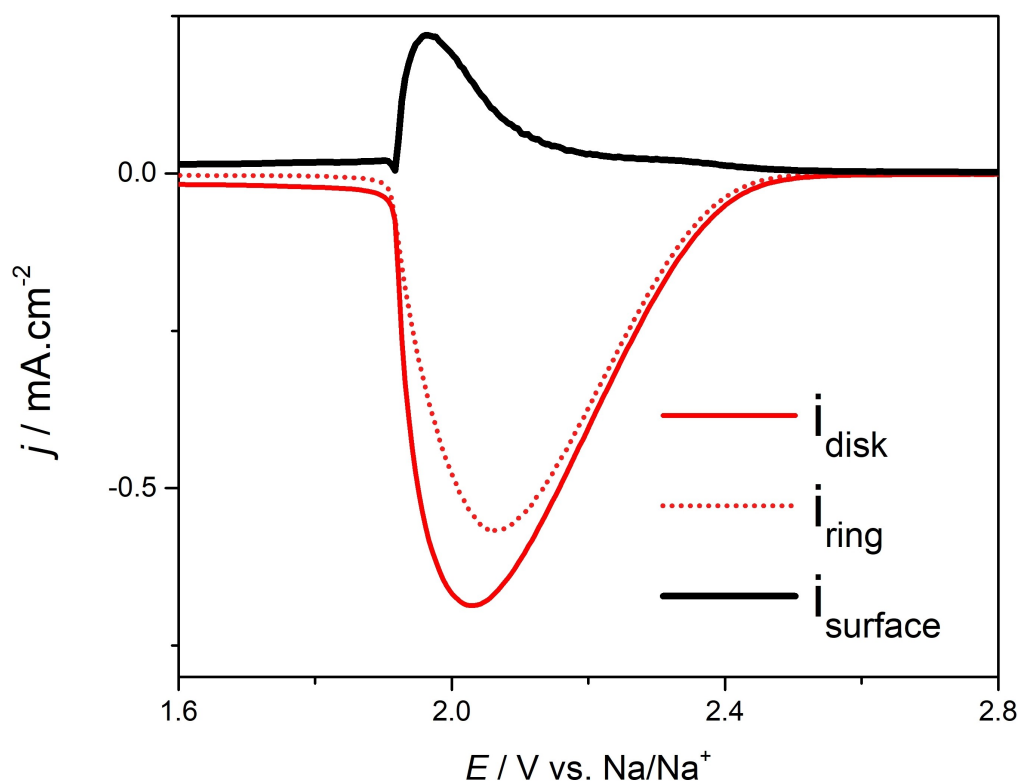
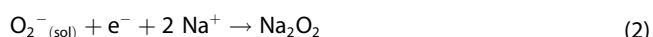
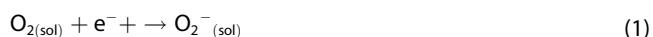


Figure 2. RRDE voltammetry in O_2 saturated 0.5 M NaOTf in DEGDM. Measurements were recorded at Au disk-Au ring electrode at a scan rate of 20 mV s^{-1} and a rotation speed of 2000 rpm. i_{disk} (red solid line) is the overall current measured, i_{ring} (red dashed line) is the current due to the formation of soluble species and i_{surface} (black solid line) is the difference between the two which is assigned to insoluble species.

for use in high resolution transmission electron microscopy (HRTEM) measurements, such that it is possible to observe any nanometer thick discharge products that form at the electrode. The cells were discharged in O₂-saturated 0.25 M NaOTf in DEGDMC at a high current density (0.4 mA cm⁻²) resulting in an overpotential of approximately 500 mV and the surface was analyzed using HRTEM, Figure 3. The images unambiguously demonstrate the formation of a 20–30 nm thick film of discharge product at the electrode surface. Previously it has been proposed that surface films of NaO₂ are responsible for sudden death at high discharge rates.^[29] This is a reasonable conclusion as neither PXRD nor X-ray photoelectron spectroscopy (XPS) analysis typically identifies Na₂O₂ in discharged electrodes. However, previous analyses of the Li⁺-ion containing system have shown that electrochemically formed peroxide is non-crystalline, explaining why Na₂O₂ may not be detected by PXRD.^[45] In addition, examination of SEM images, Figure 1, shows that NaO₂ cubes are the major discharge product in all cases making detection of trace Na₂O₂ difficult. Here we perform XPS analysis on a positive electrode discharged at a constant potential of 1.9 V vs. Na/Na⁺, where sudden death of the cell occurs. A flooded cell containing large volumes of electrolyte was used, such that much of the NaO₂ is dissolved and the relative signal for any insoluble products (i.e., Na₂O₂) is enhanced. The oxygen 1s region of the resulting spectrum is shown in Figure 3(c). The spectrum displayed a major peak centred at 530.9 eV, confirming the formation of peroxide during discharge at high overpotential.^[7,46] No peak consistent with the formation of Na₂O (529.7 eV) was observed.^[47] The peak centred at 532.9 eV is due to the formation of superoxide and appears to make up a minor contribution to the overall XPS signal.^[7] However, we reiterate that in a real cell with low electrolyte volume where NaO₂ is trapped in the electrode structure, NaO₂ is the major product, Figure S2, but only small amounts of Na₂O₂ are needed to have a detrimental impact on performance.

The data demonstrates the occurrence of two reaction processes, one at lower overpotential, which results in a soluble superoxide product and the formation of the anticipated NaO₂ cubes, and a second at a larger overpotential that results in the formation of passivating films of product that cover the electrode surface. The results are consistent with a 1e⁻ reduction of O₂ to soluble O₂⁻ stabilised by alkali ions in the solvation shell, followed by a second reduction step to Na₂O₂, Equations (1 and 2);



Onset of this second reduction will inevitably result in rapid electrode passivation and cell death and explains the trend seen during discharge of Na–O₂ cells at varying rates. These results suggest that Na₂O₂ formation is unavoidable at high overpotential presenting a challenge for the development of high-rate Na–O₂ batteries. Moreover, trace amount of Na₂O₂ could accumulate during cycling and its removal will likely

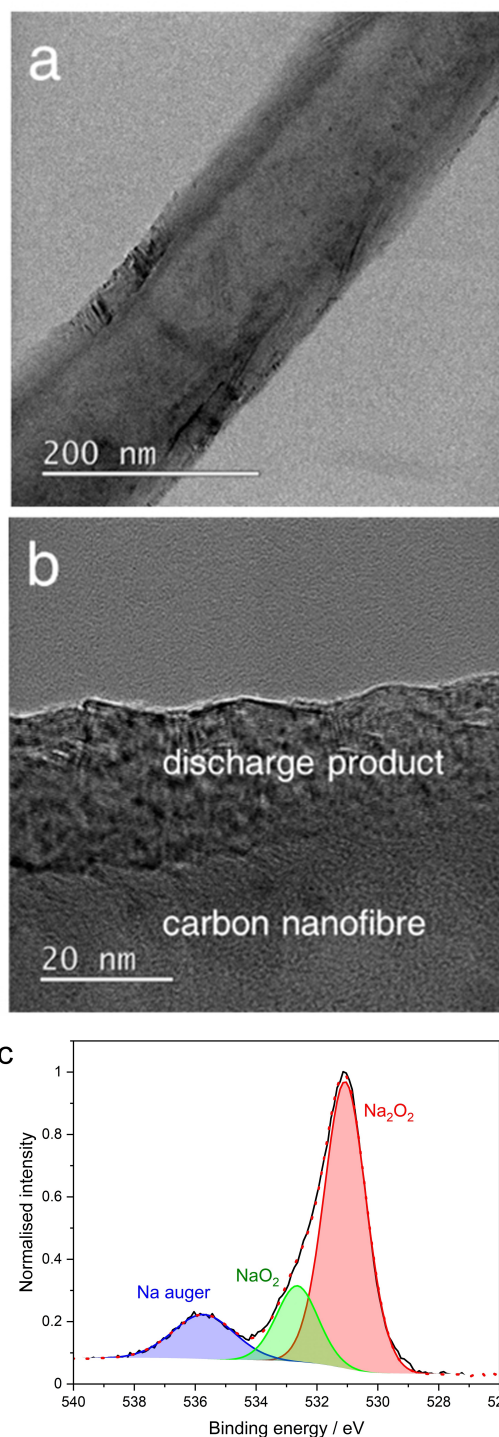


Figure 3. HRTEM images and spectroscopic analysis of the thin film product formed at the positive electrode of the Na–O₂ battery: a and b) HRTEM images showing the film deposited on carbon nanofiber electrodes during discharge at high rates (0.4 mA cm⁻²). c) X-ray photoelectron spectra in the O 1s region of Na–O₂ positive electrodes discharged at a constant potential of 1.9 V vs. Na/Na⁺. The peaks at 530.9 eV, 532.9 eV and 536 eV are due to Na₂O₂, NaO₂ and the Na auger response, respectively.

require high overpotentials during charging, eliminating many of the advantages of the Na–O₂ battery over the Li–O₂ battery. We note that changing the electrolyte solution or electrode

material would alter the potential at which Na_2O_2 forms and this could be a route to avoid its detrimental impact.

Conclusion

Here we show that the product of the aprotic oxygen reduction with Na^+ ions in glyme ethers depends on the overpotential during discharge. At low overpotential, the reaction forms the $1e^-$ reduction product NaO_2 , which is soluble in glyme-based electrolyte and results in the formation of cubic NaO_2 structures in the electrode and high capacities. At high overpotential, the reaction switches to a $2e^-$ reduction, which forms thin films of passivating Na_2O_2 across the surface of the electrode. If high rates are allowed to significantly polarise the voltage of $\text{Na}-\text{O}_2$ cells, the formation of Na_2O_2 passivating layers result in capacity limitation and rapid cell failure. To achieve high capacity and high rates, processes that result in polarisation of the electrode potential must be minimised. Practical cells will require high rates of electrochemical reduction of oxygen, together with rapid nucleation and growth of NaO_2 , and high mass-transport of oxygen and Na^+ ions, thus avoiding voltage polarisation and detrimental Na_2O_2 formation.

Experimental Section

Materials and methods

Diethylene glycol dimethyl ether (Diglyme or DEGDME) was distilled under argon over CaH_2 . The solvent was further dried for several days over freshly activated molecular sieves (type 4 Å). The final water content was ≤ 4 ppm (determined by Karl Fischer titration). Tetrabutylammonium trifluorosulfonate/triflate (TBAOTf) was recrystallised from a mixture of dichloromethane and diethyl ether and then dried under vacuum at 80°C for 3 days. Sodium triflate (NaOTf) was recrystallised from a mixture of dimethyl sulfoxide (DMSO) and dichloromethane and then dried under vacuum at 80°C for 3 days. All materials were stored in an argon glove box. High purity $\text{N}_5 \text{O}_2$ was obtained from BOC industrial gases and was used in all measurements. During measurements, O_2 was passed through a drying column consisting of freshly activated molecular sieves before entering the cell. Bubbling O_2 into the electrolyte solution for 10 mins did not change the electrolyte water content.

Electrochemical analysis

Electrochemical measurements were performed using a VMP3 electrochemical workstation (Biologic) and a multi-necked, air-tight glass cell within a glove box. Electrochemical measurements were carried out at room temperature and IR correction was used. 3 mm diameter polycrystalline Au disks (BAS Inc.) were employed as the working electrodes. Prior to use, the working electrodes were polished in a glove box with $0.05 \mu\text{m}$ alumina slurry in ethanol and rinsed with copious amounts of ethanol followed by drying under vacuum. Platinum wire served as the counter electrode. Measurements were performed using a reference electrode based on LiFePO_4 . It was first pre-oxidized (20% of total capacity) to Li_xFePO_4 , which has a constant potential. This is then placed in 0.1 M LiClO_4 in DMSO separated from the bulk electrolyte with a porous frit,

thus providing a fixed potential. Potentials were corrected to Na/Na^+ using an internal ferrocene reference and by subtracting 3.6 V. Electrolytes were saturated with O_2 . Carbon nanofibre electrodes were formed from a nanofiber, PTFE suspension in isopropanol which was cast onto stainless steel mesh, dried under vacuum, and discharged at constant current in a three-electrode cell. Rotating ring/disk electrode, RRDE, measurements were performed using a MSR rotator and a removable disk rotating ring/disk electrode containing an Au disk (5 mm diameter) and a glassy carbon ring (PINE instruments). A ring potential of 3.7 V vs. Na/Na^+ was used. Measurements were performed in a glove box in a round bottom flask and all necks other than the neck containing the shaft were sealed. The electrode was polished as described above between measurements. The collection efficiency at the ring, N , in each experiment was determined using an ideal redox couple.

$\text{Na}-\text{O}_2$ cells were built from a modified Swagelok setup. The cell was vacuum-dried under elevated temperature and transferred into a glovebox (0.1 ppm H_2O , 0.1 ppm O_2). The anode was made from metallic sodium (Sigma-Aldrich), cut into a 0.5 cm^2 disc. 0.3 mL Dried electrolyte solution (0.5 M sodium salt in diglyme) was imbibed on two Whatman glass fibre filters (QM-A grade) (dried under vacuum at 260°C , 24 h). A piece of GDL (1.13 cm^2 of surface area, $210 \mu\text{m}$ in thickness, and a weight of 10 mg) was used as cathode and held by an inox mesh current collector containing holes for gas exchange. No further insulating sleeve was used. The assembled cells were transferred from the glovebox to a filling station, and after a first evacuating step, the cells were pressurized with dry, ultrapure O_2 to 1.3 bar. To guarantee stable temperature conditions, the cells were mounted inside of a temperature-controlled incubator ($25.0 \pm 0.1^\circ\text{C}$). The electrochemical measurements were performed under temperature-controlled conditions (25.0°C) after resting for 4 h at the open-circuit voltage and using a Bio-Logic VMP3 potentiostat.

Characterization

X-ray photoelectron spectroscopy was performed on a Thermo Scientific K-Alpha X-ray photoelectron spectrometer (XPS) instrument equipped with a microfocussed monochromated Al X-ray source. The source was operated at 12 keV and a 400 micron spot size was used. The analyser operates at a constant analyser energy (CAE) 200 eV for survey scans and 50 eV for detailed scans. Charge neutralization was applied using a combined low energy / ion flood source. Powder X-ray diffraction (PXRD) measurements were performed by washing samples with dried diglyme prior to PXRD analysis. A Bruker D8 Advance diffractometer with a $\text{Cu } K_\alpha$ radiation source ($\lambda_1 = 1.5405 \text{ \AA}$, $\lambda_2 = 1.5443 \text{ \AA}$) and a Lynxeye XE detector was used to collect the PXRD patterns. The PXRD patterns were recorded for 30 min in the 2θ range of 20° – 65° . A special airtight cell with a beryllium window was used to guarantee no ambient air contamination during PXRD measurements.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

Keywords: diglyme · oxygen reduction reaction · passivating films · sodium peroxide · sodium superoxide

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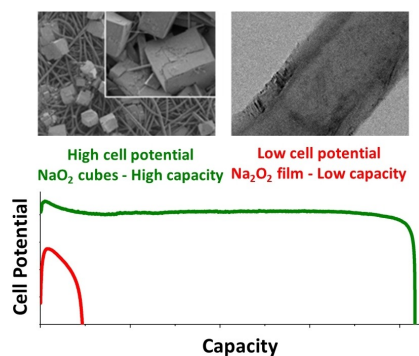
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RESEARCH ARTICLE

Na₂O₂ matters: Sodium-air battery discharge capacities are limited at high rates and sudden death of the cell is typically observed. Here we use a combination of spectroscopic and electrochemical analyses to confirm the generation of Na₂O₂ during O₂ reduction in the cell. Electron microscopy demonstrates that this insulation alkali oxide forms as thin films on the electrode, which lead to premature cell death. This highlights a key chemical limitation for Na–O₂ battery performance and the need to avoid 2-electron reduction of oxygen in the battery.



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Competitive Oxygen Reduction Pathways to Superoxide and Peroxide during Sodium-Oxygen Battery Discharge

