Effect of charging protocol and carbon electrode selection in Na–O2 batteries

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Nonaqueous sodium- and lithium-oxygen batteries are of interest because of their high theoretical specific energies relative to state-of-the-art Li-ion batteries. However, several challenges limit rechargeability, including instability of the carbon electrode and electrolyte with reactive oxygen species formed during cycling. This work investigates strategies to improve the cycling efficiency of the Na–O2 system and minimize irreversible degradation of electrolyte and electrode materials. We show that charging cells with a constant current/constant voltage (CCCV) protocol is a promising technique made possible by the slight solubility of sodium superoxide in nonaqueous electrolytes. In addition, the type of carbon electrode has a significant impact on cell performance and efficacy of the cycling protocol. Graphitic carbon electrodes coupled with CCCV charging demonstrate higher reversibility, more efficient oxygen evolution, and less outgassing than conventional cells using a porous carbon paper electrode and only a constant current charge.

Introduction

Finding efficient energy storage technologies has become increasingly important as the global energy economy shifts from fossil fuels to renewable energy generation and storage. In addition, the proliferation of electric vehicles and portable consumer electronics has prompted research into next generation, rechargeable batteries. Of the various "beyond-Li-ion" chemistries being investigated, nonaqueous metal-air systems offer high theoretical energy densities. The nonaqueous Li–O2 system has the highest theoretical energy density owing to the formation of the two-electron discharge product lithium peroxide (Li2O2) [1–3]:

\[
\text{Li}^+ + \text{O}_2 + 2e^- \leftrightarrow \text{Li}_2\text{O}_2 \quad U^\circ = 2.96 \text{ V vs. Li/Li}^+ \quad (1)
\]

\(U^\circ\) is the equilibrium potential of the cathode reaction at standard conditions. The discharge reaction occurs with relatively high efficiency; however, the charging process results in a much lower evolution of O2 gas than expected and occurs at high overpotentials that induce other degradation processes [4–6]. Though the Na–O2 system has a lower energy density than its Li–O2 counterpart, 1100 Wh/kg NaO2 versus 3460 Wh/kg Li2O2, respectively, the improved oxygen evolution and low overpotentials for most of charge demonstrate a more reversible chemistry [7, 8]. In nonaqueous, glyme-based solvents, Na–O2 cells form a one-electron reduction product, sodium superoxide (NaO2) [9, 10]:

\[
\text{Na}^+ + \text{O}_2 + e^- \leftrightarrow \text{NaO}_2 \quad U^\circ = 2.27 \text{ V vs. Na/Na}^+ \quad (2)
\]

One barrier to the success of metal–air systems is the insolubility and insulating nature of the solid oxide discharge product [11, 12]. Once formed, these oxides coat the cathode and form a passivating layer, which increases overpotentials and induces cell death much before the available capacity is reached. Na–O2 cells exhibit better reversibility and fewer side products than Li–O2 cells, owing in part to the slight solubility of sodium superoxide in the organic electrolyte [10]. Several studies suggest that sodium superoxide forms via two related mechanisms: (1) electrochemical oxygen reduction on the surface of the electrode inducing Na2O2 deposition as a thin film and (2) chemical dissolution of NaO2 into the electrolyte and precipitation as micron-sized cubes which are easily observed via SEM [10, 13, 14]. It is the sparing solubility of NaO2 that allows this second solution-based mechanism to occur. In Li cells, however, the insolvability of Li2O2 in the ethereal electrolyte prevents any
observable dissolution from the electrode surface without the use of solvating additives or different solvents [11, 15–17].

Nichols et al. previously showed that cell death on both discharge and charge in Na–O₂ systems is a function of the current rate drawn [10]. When charging at low current rates, NaO₂ films undergo oxidation on the surface of the electrode while bulk NaO₂ from the large cubes dissolves and diffuses to the electrode surface where it is electrochemically consumed. These low currents on charge result in larger capacities before the onset of cell death. As the current rate increases, the surface films oxidize faster and the current begins to rely on the dissolution of NaO₂ in the large cubes, followed by diffusion to the electrode surface. When the dissolution or diffusion rate cannot maintain the current, the overpotential increases, enabling other oxidation reactions, typically irreversible degradation processes involving the electrolyte or carbon cathode [18].

In this work, we employ the insight from Nichols et al. to study a constant current/constant voltage (CCCV) charging technique wherein the potential is held constant to allow dissolution and diffusion of NaO₂ to dictate the current rate. Charging using CCCV is standard practice in Li-ion batteries in order to prevent the plating of lithium metal on graphite at high overpotentials [19, 20]. We show it can also be used in metal–air batteries to prevent oxidation of the carbon electrodes or electrolyte during charge. We also compare this charge protocol in Na–O₂ cells and LiO₂ cells to show the importance of product solubility (noting again that NaO₂ has slight solubility in ethereal electrolytes, whereas Li₂O₂ is insoluble) in allowing CCCV to be used beneficially. With this charging method, cells using a carbon paper electrode demonstrate comparable oxygen evolution and charge capacity to cells charged galvanostatically. When operating the cell with graphitic carbon electrodes, this charging protocol offers a significant improvement in oxygen evolution and a decrease in gaseous side products compared to standard constant current charging even over multiple cycles, highlighting the importance of coupling electrode selection with charge protocol in improving reaction reversibility.

Results and discussion

P50 carbon paper electrode

Figure 1 shows electrochemical cycling data and gas consumption and evolution over multiple cycles for cells constructed with porous P50 carbon paper electrodes. P50 electrodes have been
used in previous reports on Na–O2 and Li–O2 batteries as well as in fuel cell literature given their high porosity for gas transport, large electrochemically active surface area, and convenience of use [21]. In Fig. 1(a), in which the cell is cycled with constant current, the cell maintains a low ∼100 mV overpotential for most of charge, followed by a precipitous increase in overpotential. Gas consumption and evolution data follow the theoretical linear relationship of 1 electron per O2 molecule, indicating that Eq. 2 is the dominant electrochemical process. High overpotentials at the end of charge suggest that the easily oxidized films have been consumed, and that the current now relies on the dissolution and diffusion of NaO2 to the electrode surface, as well as parasitic oxidative reactions that result in less gas evolved than expected towards the end of charge [10]; this is most clearly observed towards the end of the 3rd and 4th charge.

In the CCCV charging scheme [Fig. 1(b)], once the onset of cell death is reached, the potential is held at 3V until the current decays to 15 μA. The potential hold allows NaO2 contained in large deposited cubes to diffuse to the electrode surface, allowing the cells to be nearly fully charged on a capacity basis (i.e., the full discharge capacity is >99% recovered on the subsequent charge). This behavior is unique to the Na–O2 system due to the slight solubility of NaO2 in ethereal electrolyte. In Li–O2 cells, charging with CCCV does not result in full capacity recovery at ∼700 mV overpotentials [comparable overpotentials to those shown in Fig. 1(b)] because Li2O2 is insoluble and therefore cannot readily diffuse to the electrode surface (Fig. 2). In this lithium cell, LiNO3 in the electrolyte induces growth of micron-sized platelets of Li2O2 during discharge, thereby increasing cell capacity over electrolytes in which platelet growth is not observed [16]. Most Li2O2 in these large structures is electronically isolated from the surface, so the dissolution and diffusion mechanism must be activated in order to recover the full capacity of the cell. This Li–O2 system, which is entirely analogous to the Na–O2 system presented in Fig. 1(b), charges to 48.7% of its discharge capacity (1 mAh) and results in an oxygen evolution to oxygen reduction (OER/ORR) ratio of 0.43. This charging method took 11.6 h, significantly longer than the 2 h required for a constant current charge. These cycling inefficiencies in the lithium system demonstrate fundamental challenges for improving capacity and cyclability of the Li–O2 battery; in the sodium system, however, we observe better cyclability and cell performance with a CCCV charging protocol.

In CCCV charging [Fig. 1(b)], the cell reaches 99% of the capacity expected by the 15 μA cutoff current during the CV portion and results in an oxygen evolution to oxygen reduction ratio of 0.91 ± 0.01, comparable to that of CC charging without a cutoff voltage. Additional metrics are summarized in Table 1 (graphite electrodes are discussed below) and demonstrate very similar performance of the two charging schemes. While CCCV charging may prevent high at a nearly ideal rate of 1 e−/O2, as expected given Eq. 2, for all cycles in each cell. During charge, gas evolution begins to deviate from ideality about halfway through CC charging. The ∼4 μmoles of lost oxygen at the end of the first charge is accounted for by a lower than expected yield of NaO2 on the first discharge, as confirmed by iodometric titrations (33 ± 2 μmol vs. the theoretical value of 37 μmol.) These results indicate small amounts of NaO2 react irreversibly on cycling, so inevitable oxygen loss may limit the efficacy of optimizing the charging protocol. However, as will be shown below, the choice of cathode material impacts the amount of irreversible degradation products formed during charge.

Figure 2: Cycling data for a Li–O2 cell charged using the CCCV technique. Voltage (blue line), current (orange dashed), and gas consumption and evolution (blue circles) are all plotted against capacity. The cell was discharged at 0.5 mA for 2 hours, charged at 0.5 mA until 3.7 V, and held at constant voltage until the current decayed to 15 μA.
In an attempt to understand the $O_2$ losses observed in Fig. 1, we note that sodium carbonate ($Na_2CO_3$) is known to form on discharge in $Na-O_2$ cells [7], so carbonate titrations were performed to measure the amount of $Na_2CO_3$ over multiple cycles of charging via CC and CCCV (Table 2, graphite electrode results are discussed below).

Over the course of three discharge and charge cycles, carbon paper electrodes cycled with CCCV accumulate more $Na_2CO_3$ than those cycled with CC. Since the potential is held at a lower value at the end of charge during CCCV, surface carbonates are not as readily oxidized by either the electrode or the reactive species generated at high potentials. In CC charging, these carbonate species are oxidized at the end of charge and generate $CO_2$ as shown in the DEMS results (Fig. 3). Results from the graphitic electrodes will be discussed in a subsequent section.

**DEMS results**

To quantify the specific gases evolved in this system, the differential electrochemical mass spectrometer (DEMS) instrument samples the cell headspace during charge. Figure 3 shows the voltage profiles and molar flux of gases evolved during CC and CCCV charging protocol with cells containing a P50 carbon paper electrode. All cells demonstrate oxygen evolution flux close to the theoretical $1e^-/O_2$ rate for the majority of charge. At the end of charge in constant current cycling, the oxygen evolution declines as hydrogen and carbon dioxide form upon the sudden increase in cell voltage. On the second cycle, these degradation products form at more appreciable rates.

Charging with CCCV generates much lower quantities of $H_2$ or $CO_2$. On the second cycle, the CC cell again generates decomposition products at the end of charge, while the CCCV cell does not. The source of carbon dioxide is not entirely clear given that there are several carbon-containing species in the battery, including the ethereal electrolyte and the porous carbon electrode. One proposed mechanism suggests DME can undergo hydrogen abstraction by reactive oxygen species and decompose to sodium carbonate [22]. At high potentials, this species can be oxidized, generating carbon dioxide gas. Hydrogen gas is likely a reduction product at the sodium electrode as a result of protons formed from electrolyte degradation at the cathode during high overpotential operation.

The percentage of hydrogen and carbon dioxide off-gassed from the battery as a function of cycle number and charging method is summarized in Fig. 4. The CCCV charging method significantly decreases gaseous side product formation over both cycles. While this low gas evolution is in part due to the limited oxidation of solid carbonate species on the electrode surface (as seen from the small accumulation of carbonates with cycling in Table 2), it also indicates the benefit that maintaining low overpotentials through the end of charge provides on the stability of the cell.

**Graphite electrode**

Unavoidable capacity loss due to reaction of $NaO_2$ on discharge and continual formation of sodium carbonate limits the reversibility of the $Na-O_2$ system. Previous work suggests that the type of carbon electrode plays a role in product morphology and cell performance [23]. In hopes of improving reaction reversibility, we synthesized and tested graphitic electrodes with our CCCV charging scheme and the aforementioned characterization tools. Given the heterogeneous nature of the P50 carbon paper, we hypothesized that the more crystalline lower surface area graphite would result in improved reversibility because there are fewer susceptible surface sites for reactive oxygen attack.

Figure 5 shows electrochemical cycling and gas consumption and evolution data for sodium cells constructed with graphitic electrodes. Similar to the carbon paper electrodes, the near $1e^-/O_2$ gas consumption confirms that $2$ is the dominant electrochemical reaction in this system. During CC charging (a), gas evolution deviates from ideality at the end of the first charge, similar to behavior observed with P50 carbon paper electrodes. Subsequent cycles suffer from significant discharge capacity loss. It is possible that these high overpotentials induce oxidative side effects.

| TABLE 1: Comparison of first-cycle CC and CCCV charging techniques in Na–O2 cells with P50 carbon paper and graphitic electrodes. |
|---------------------------------|---------------|---------------|---------------|---------------|
| Carbon paper electrode | Graphite electrode |
| CC | CCCV | CC | CCCV |
| OER/ORR (μmol/g of carbon) | 0.90 ± 0.02 | 0.91 ± 0.01 | 0.94 ± 0.02 | 0.95 ± 0.01 |
| $e^-/O_2$ on charge | 1.08 ± 0.02 | 1.11 ± 0.03 | 1.07 ± 0.02 | 1.04 ± 0.01 |
| Charge capacity (mAh) | 1.0 | 0.99 ± 0.004 | 1.0 | 0.97 ± 0.01 |
| Time to charge (h) | 1.0 | 2.8 ± 0.4 | 2.0 | 5.9 ± 0.8 |

Titrations occurred on cathodes extracted from cells at the top-of-charge.

| TABLE 2: Amount of $Na_2CO_3$ (μmol/g of carbon) formed after 3 cycles with CC or CCCV charging. |
|---------------------------------|---------------|---------------|
| Carbon paper electrode | Graphite electrode |
| CC | CCCV | CC | CCCV |
| $Na_2CO_3$ (μmol/g of carbon) | 77.5 ± 27 | 134.8 ± 46 | 20.5 ± 1.3 | 34.4 ± 3.0 |

Titrations occurred on cathodes extracted from cells at the top-of-charge.
reactions that involve oxidation of the graphite, thereby forming insoluble, electronically insulating species on the graphitic electrode surface that limit the electrochemically active surface area on which oxygen can be reduced in following cycles. The higher electrochemically active surface area of carbon paper as well as increased porosity relative to graphitic electrodes may explain why this capacity fade on discharge is not seen in the previous case with carbon paper electrodes.

The improved cyclability of this graphite-based cell using CCCV demonstrates the benefit of lower charging overpotentials. Cycling with CCCV (Fig. 5b) results in better gas evolution/consumption reversibility and prevents discharge capacity fade on subsequent cycles. In fact, this charging protocol in combination with the graphite electrodes exhibits the best oxygen reversibility of all electrodes and cycling protocol measured, as indicated by the lowest cumulative oxygen loss over 4 cycles (8 μmols).

Degradation of carbon-containing species in these cells contributes to the formation of sodium carbonate on the graphitic electrodes, albeit to a much lesser extent than the carbon paper electrodes. Table 2 summarizes the results of carbonate titrations performed on electrodes after 3 discharge–charge cycles. Similar to the P50 carbon paper system, graphitic electrodes accumulate more Na₂CO₃ when charged with the low-voltage CCCV method. Because the carbonates on the electrodes experience lower oxidative overpotentials at the end of CCCV charge, there is less driving force for the oxidation of the carbonate species to CO₂. P50 carbon paper electrodes form greater amounts of Na₂CO₃ per mass of carbon than graphite electrodes. This behavior is likely caused by two factors. First, it is known that lower surface area electrodes tend to limit parasitic side reactions [24], implying that the lower surface area graphite electrodes should yield fewer side products. Second, P50 carbon surface is likely to be highly defective (i.e., contain dangling C–H and C–O bonds) compared to the graphite
particles. These defects likely catalyze the efficient formation of reactive species that degrade the electrolyte, or perhaps are vulnerable themselves to attack from reactive species. In other words, the lower surface area and more ordered surface structure of the graphite particles both likely result in improved reaction reversibility compared to P50 carbon paper.

DEMS measurements were also performed to determine gaseous side products formed during charge. Figure 6 shows the oxygen, carbon dioxide, and hydrogen evolution rates during charge on the first two cycles using both charging methods. Measurable hydrogen and carbon dioxide formation occurs during CC charging once the potential reaches 4V, and, importantly, oxygen evolution continuously decreases once the high voltage plateau is hit, suggesting that parasitic reactions start to dominate at high voltages. This behavior is not seen when charging with CCCV, where oxygen evolution dominates the total gas evolution in the system, again indicating the improvement to cycling reversibility imparted by CCCV.

The amount of gaseous side products evolved during the DEMS experiments are calculated in Figure 7. When charging with CCCV, the second cycle produces less H₂ and CO₂, indicating that parasitic reactions slow over time with CCCV cycling. In contrast, cells cycled galvanostatically generate a considerable quantity of side products in the first cycle, which only increases in the subsequent cycle. Cell performance metrics for the graphitic electrode system are summarized in Table 1. The graphite system shows improvements over the P50 carbon paper electrodes in OER/ORR and e⁻/O₂ on charge. By preventing high overpotentials, the CCCV charging decreases the rate of oxidative side reactions that degrade the battery and negatively impact its oxygen evolution efficiency. In cells made with graphitic electrodes, the chronoamperometric charging technique offers a much improved pathway to long-term cyclability.

Conclusion
A CCCV charging protocol can be amenable to metal–air batteries in which the discharge product is soluble. We demonstrated that NaO₂, a sparingly soluble discharge product, is oxidized at low overpotentials when allowed time to dissolve and diffuse to the electrode surface. This evidence further corroborates the solution-based mechanism of crystal growth and dissolution in
Na–O₂ cells. The lower overpotentials of the constant current-constant voltage charging method also appear to reduce both degradation of the electrolyte and promotion of other deleterious side reactions. Furthermore, sodium–air cells constructed with graphitic electrodes retained discharge capacity and evolved lower amounts of gaseous side products over multiple cycles when charged using the CCCV technique. While this study has shed insight on how to use solubility to the advantage of cell cycling, there are several barriers that impede its successful application in real battery systems. Further optimization of graphite electrode synthesis is needed to increase porosity and surface area for improved gas diffusion, higher discharge capacity, and lower charge time. Unavoidable capacity loss due to reaction of NaO₂ on discharge and continual formation of sodium carbonate on the carbon electrode limit reversibility of this system. Future electrode and materials engineering should work to mitigate these side reactions to enable long-term cycling.

**Experimental methods**

**Materials and cell assembly**

Sodium trifluoromethanesulfonate (NaOTf) and lithium nitrate (LiNO₃) were purchased from Sigma Aldrich and dried in a vacuum oven overnight at 80 °C before use. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and 1,2-dimethoxyethane (DME) from BASF were used as received. Na metal was purchased from both Gallium Source and Sigma Aldrich. Avcarb P50 carbon paper from Fuel Cell Earth was rinsed with isopropanol and acetone and dried overnight in a vacuum oven at 120 °C before bringing into an Ar-filled glovebox and heating to 120 °C. MesoCarbon MicroBead (MCMB) graphite powder (average diameter = 17.6 μm, surface area = 2.0 m²/g) was purchased from MTI Corporation. Vulcan XC72 was purchased from Fuel Cell Store. A dispersion of 60wt% polytetrafluoroethylene (PTFE) in water (Sigma Aldrich) was used as the binder in the graphitic electrodes.
Na–O₂ electrochemical cells were constructed with a sodium metal electrode, a 1/2" diameter Whatman quartz microfiber (QMA) separator, an 11 mm diameter carbon electrode, electrolyte, and a stainless steel spacer which allowed a known volume of gas to collect in the headspace. The modified Swagelock-type electrochemical cell design has been described previously [25, 26].

Na metal was rolled between pieces of Celgard 2500 to form a thin foil, which was punched into 11 mm diameter disks. The electrolyte used for all Na cells in this study was 80 μL of 0.5M NaOTf in DME. P50 carbon paper electrodes were cut into 11 mm diameter disks, weighing 4.8mg. In cells with P50 carbon paper electrodes, a 12 mm diameter stainless steel mesh was also placed between the carbon and spacer to improve electronic contact.

The graphitic carbon electrodes were synthesized by combining MesoCarbon MicroBead graphite powder and PTFE (60w/w% in water) in a 90:10 w/w ratio in a solution of water and IPA in a 4:1 volume ratio. The total solids content was 5w/v% in the solution. The mixture was sonicated and then stirred for 30 min. The solvent was evaporated over several hours at 70 °C until a thick slurry remained. The slurry was cast onto 11 mm diameter stainless steel meshes and dried overnight in a vacuum oven at 110 °C. The graphite loading on each electrode ranged from 19 to 29 mg.

Li cells were constructed with a 11 mm Li metal electrode, QMA separator, 12 mm diameter Vulcan XC72 carbon electrode, stainless steel spacer, and 0.5M LiNO₃, 0.5M LiTFSI in DME electrolyte. This carbon electrode was made by spray coating a 75:25 w/w mixture of carbon to PTFE binder onto stainless steel mesh and has been described previously [16].

### Electrochemical cycling

Cycling using a constant current (CC) protocol was performed on cells comprised of either a P50 carbon or graphitic carbon cathode. In both, the cell was discharged at 0.5 mA for 2 h and allowed to rest for 30 min. In P50 carbon cells, the cell was charged at 1 mA for 1 h. In graphitic carbon cells, the cell was charged at 0.5 mA for 2 h. Using these charge rates, we found that overpotentials on the large charge plateau were within 200 mV between the two carbon electrodes. We estimate that our P50 carbon electrodes had a total surface area of 425 cm² (given 88 cm²/mg, as previously reported [27]). The surface area of our graphitic electrodes was more challenging to calculate, as we expect the PTFE binder to block porosity and coat the graphite surface to some extent (note that P50 carbon paper is free-standing and binder-free). A typical 25 mg graphite electrode will have 500 cm² of calculated surface area without any binder. Given that we find similar overpotentials between P50 and graphite with half the current density on graphite, we anticipate that the active graphite surface area is roughly half that of the P50, implying that PTFE binder limits access to roughly half of the graphite surface area.

In the constant current/constant voltage (CCCV) charging scheme, cells were discharged and rested as described above. The cells were then charged initially at a constant current until the onset of cell death, defined as 3V, at which point the voltage was held at 3V until the current decayed to the cutoff value. For studies with P50 porous carbon cathodes, this cutoff current was 15 μA. For studies with graphitic carbon cathodes, the cutoff current was 5 μA. This voltage hold allows the diffusion of NaO₂ from electronically isolated surfaces to dictate the current the cell is able to draw. In P50 carbon cells, the charge current was 1 mA, whereas the graphitic cells required a lower charge current of 0.5 mA due to their lower surface area as described above. Faster currents in the graphitic cells increased the likelihood of sodium dendrite formation, short circuiting, and cell failure.

### Gas analysis & product characterization

The hermetically sealed Swagelock-type cells with gas capillaries allowed the quantitative measurement of oxygen consumption and gas evolution during cycling. The headspace was pressurized with 1150–1200 torr of oxygen and closed in order to monitor the pressure decay and rise. The differential electrochemical mass spectrometer (DEMS) allowed quantification of oxygen, carbon dioxide, and hydrogen gases released during charge. The headspace was filled with Ar before charging and swept periodically into the mass spectrometer to determine the identity and quantity of gases released during charge. These methods have been described in detail previously [2].

Ex situ titrations have been used in prior studies to measure lithium carbonate and lithium hydroxide on cathode surfaces in lithium-ion cells, and we employed a similar procedure here to measure analogous species in Na–O₂ cells [28]. Sodium carbonate (Na₂CO₃) titrations were performed on carbon electrodes extracted in an Ar environment, rinsed with DME to remove salts, and dried in a vacuum antechamber. 5 mL of degassed water was added to the electrode, converting any NaO₂ to NaOH and dissolving Na₂CO₃ into solution. The solution was then filtered to remove particulate carbon that may interfere with the titration. Phenolphthalein was added and an acid-base titration was performed with 0.1M HCl via the two subsequent reactions:

\[
\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O} \quad (3)
\]

\[
\text{Na}_2\text{CO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{NaHCO}_3 \quad (4)
\]

Once the solution was titrated from pink to clear, a second indicator, methyl red-bromocresol green, was added and the solution was titrated with HCl from a blue to a red endpoint.
NaHCO₃ + HCl → NaCl + H₂O + CO₂  \hspace{1cm} (5)

The volume of HCl from the second titration was used to calculate the amount of Na₂CO₃ originally present, while the volume from the first titration included both the amount of Na₂CO₃ and NaOH present, so the amount of NaOH, and therefore NaO₂, could also be calculated. Care was taken to prevent exposure to air which can contaminate samples with additional carbonates from atmospheric CO₂.

Iodometric titrations have been used in metal–air systems in order to determine the amount of superoxide or peroxide species remaining on the carbon electrode [5, 22, 29]. These titrations were used to compare the amount of sodium superoxide at various states of charge using the two techniques. After cells were cycled, the cell headspace was flushed with Ar gas to remove O₂ and brought into an Ar-containing glovebox. The carbon electrode was extracted, rinsed with DME, and dried under vacuum in the glovebox antechamber in order to remove the electrolyte solvent, which is known to undergo hydrogen abstraction by reactive oxygen species like peroxides and superoxides and can interfere with the results of the titration. Once removed from the glovebox in an Ar-containing septum vial, 2 mL of water was added to the cathode. Upon addition of water, NaO₂ readily disproportionates by the following reaction:

2NaO₂ + 2H₂O → 2NaOH + H₂O₂ + O₂ \hspace{1cm} (6)

Then, potassium iodide was added and underwent oxidation by H₂O₂ in an acidic environment with a molybdate catalyst to form iodine:

H₂O₂ + 2KI + H₂SO₄ → I₂ + K₂SO₄ + 2H₂O \hspace{1cm} (7)

The iodine dissolved in solution turned the solution pale yellow. It was then reduced by titrating the solution with sodium thiosulfate until the solution became colorless:

I₂ + 2Na₂S₂O₃ → Na₂S₄O₆ + 2NaI \hspace{1cm} (8)

The amount of sodium thiosulfate added was correlated via a 1:1 molar relationship to the amount of sodium superoxide originally present in the cathode.

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