Supporting Information

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

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cssc_201600034_sm_misellaneous_information.pdf
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<table>
<thead>
<tr>
<th>NaO$_2$</th>
<th>33.9 (± 0.50)</th>
<th>1.80 (± 0.20)</th>
<th>0.37 (± 0.10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$CO$_3$</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Na$_2^{13}$CO$_3$</td>
<td>0.06 (± 0.02)</td>
<td>0.26 (± 0.06)</td>
<td>0.17 (± 0.06)</td>
</tr>
<tr>
<td>Sodium formate</td>
<td>0.6</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Sodium acetate</td>
<td>1.3</td>
<td>1.5</td>
<td>1.3</td>
</tr>
<tr>
<td>Methoxy (oxo)acetic anhydride</td>
<td>0.6</td>
<td>0.4</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table S2. Absolute amounts in μmols of NaO$_2$ and degradation products after discharge of different carbon electrodes to 1 mAh capacity. The theoretical amount of NaO$_2$ is 37.7 μmols. Error in NaO$_2$ determination by iodometric titration is estimated to be ± 0.50. Error in the other values is difficult to estimate owing to the combination of methods used, but is on the order of 10-20%.

<table>
<thead>
<tr>
<th></th>
<th>NaO$_2$</th>
<th>Na$_2$CO$_3$</th>
<th>Na-formate</th>
<th>Na-acetate</th>
<th>Methoxy (oxo)acetic anhydride</th>
</tr>
</thead>
<tbody>
<tr>
<td>13C-carbon</td>
<td>33.9</td>
<td>0.5</td>
<td>0.6</td>
<td>1.3</td>
<td>0.6</td>
</tr>
<tr>
<td>Freudenberg</td>
<td>36.2</td>
<td>0.2</td>
<td>Trace</td>
<td>0.3</td>
<td>Trace</td>
</tr>
<tr>
<td>Vulcan</td>
<td>32.8</td>
<td>0.9</td>
<td>Trace</td>
<td>3.9</td>
<td>1.1</td>
</tr>
</tbody>
</table>
Experimental Details: iodometric titration to determine NaO₂ content

The chemical reactions involved in the quantification of sodium superoxide on the cathode are the following:

\[ 2\text{NaO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2\text{O}_2 + \text{O}_2 \]  
(1)

\[ \text{H}_2\text{O}_2 + 3\text{I}^- + 2\text{H}^+ \leftrightarrow 2\text{H}_2\text{O} + \text{I}_3^- \]  
(2)

\[ \text{I}_3^- + 2\text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI} \]  
(3)

In a chemical reaction involving H₂O₂ and I⁻ (2), the former is reduced to water and the latter is oxidized to iodine, which can then be titrated using standard thiosulfate solution to quantify the peroxide concentration. The net reaction between peroxide and iodide is as shown in (2). This reaction is slow without a catalyst but can be quite fast in the presence of catalysts such as Mo(VI) and excess I⁻ that forces the reaction to the right resulting in the formation of I₃⁻. The I₃⁻ is titrated using thiosulfate based on the following reaction:

\[ \text{I}_3^- + 2\text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI} \]

In a standard iodometric estimation of H₂O₂, the peroxide is reacted with excess iodide in acidic media, but acid is known to cause chemical disproportionation of peroxide to water and oxygen. Furthermore, iodide is prone to oxidation in air at acidic pH. Both these processes are likely to introduce significant error in the peroxide quantification. To circumvent this, a molybdenum catalyst in NH₄OH/NH₄NO₃ solution has been utilized. In our work, we have adopted an modified iodometric method that instead employs a pH neutral iodide-phosphate buffer reaction media to maintain a steady supply of protons for the peroxide-iodide reaction, while maintaining a constant pH. A neutral pH suppresses peroxide disproportionation and decelerates the oxidation of iodide. The inhibition of iodide oxidation was evident from the unchanged color of the post titration solution (colorless) even days after the titration. In a standard iodometric procedure, the post titration solution turns blue very quickly from the oxidation of I⁻ to I₂ which in turn, binds to starch to give the blue color.

The buffer-catalyst solution was prepared by dissolving 65 mg of (NH₄)₆Mo₇O₂₄ •4H₂O (ammonium heptamolybdate) along with 0.11 mol of H₂PO₄⁻ and 0.03 mol of HPO₄²⁻ in 500 ml of water. Adding 67 g of KI to this buffer solution and diluting it to 1 L resulted in the reagent buffer solution, which was freshly prepared before use. For the NaO₂ quantification, the discharged/charged cathodes were transferred to a glass vial into which 5 ml of water was added. After vigorous shaking, the content of the vial was transferred to a conical flask with an extra 5
ml of water that was used to rinse the vial. To this mixture, 15 ml of water and 25 ml of buffer catalyst solution was added. The mixed solution immediately turned yellow indicating the liberation of iodine, which was titrated with standardized thiosulfate solution till a straw yellow color was achieved. The titration was continued after adding starch indicator solution with the end point showing a color change from blue-violet to colorless.
Figure S1. Powder x-ray diffraction pattern of a $^{13}$C cathode after discharge to 1 mAh in 0.5M NaOTf/15 ppm H$_2$O/diglyme. The pattern is indexed to the cubic phase NaO$_2$. 
Figure S2 – C1s XPS spectra for $^{13}$C positive electrodes electrochemically discharged to a capacity of 1 mAh (a), and then charged to a voltage limitation of 3.0 V (b) or 4.4 V (c). All electrodes were operated in 20 ppm H$_2$O/0.5M NaOTf/DEGDME. These electrodes were washed in THF and dried prior to analysis.
Discussion of Figure S2

The products on the electrode surface, without any post-mortem treatment except for a THF wash, were also examined by XPS to complement the studies reported in the main text. The C1s spectra of an electrode discharged (Figure S2a), charged to 3.0 V (Figure S2b), and charged to 4.4 V (Figure S2c) reveals the electrode surface is covered with carboxylate decomposition products (formate, acetate, acetic anhydride), identified by comparison with literature references.\(^2\) The dominant signal for all electrodes (apart from sp\(^3\) carbon in the electrode at 284.8 eV which serves as an internal reference) is that of C-O-Na (~285.5 eV), indicative of formate/acetate coverage on the electrode surface. This is the same conclusion determined from the quantitative analysis presented in the main body of this report. The absolute area of this signal is within 10% for all three electrodes studied. The signals at ~290 eV correspond to the C=O groups of sodium acetate/formate and sodium carbonate, another degradation product identified previously, as well as C-F carbon from the PTFE binder (~294.5 eV and 292 eV).\(^2\) The C1s signals for the discharged electrode are at slightly higher binding energies than those for the charged electrodes. The abundance of insulating NaO\(_2\) that covers the electrode surface leads to this shift. Overall, the results are consistent with the nature of the NaO\(_2\) surface as a highly active site for electrolyte degradation. On charge, a great majority of this NaO\(_2\) is removed (Figure 3, main text), and hence the electrode surface is primarily conductive carbon.
Figure S3 - O1s XPS spectra for $^{13}$C positive electrodes electrochemically discharged to a capacity of 1 mAh (a), and then charged to a voltage cutoff of 3.0 V (b) or 4.4 V (c). All cells were operated in an electrolyte of 20 ppm H$_2$O/0.5M NaOTf/DEGDME. The electrodes were washed in THF and dried prior to analysis.
Discussion of Figure S3

XPS was also used to investigate the formation and removal of NaO$_2$ on charging of the cell. On discharge, fitting of the O1s spectra (Figure S3a) reveals mostly NaO$_2$, identified from the characteristic binding energy of O$_2^-$ at 532.2 eV.$^{2,3}$ This peak is accompanied by a second feature at ~ 534 eV that is characteristic of C-O from carboxylate products, also identified in the C1s spectra (Figure S2). Because of the abundance of NaO$_2$ after discharge, the signal ratio of NaO$_2$ to C-O is very large. On charge to 3.0 V, the signal corresponding to NaO$_2$ diminishes in proportion to the C-O characteristic peak, indicating that the surface NaO$_2$/carboxylate ratio becomes lower as NaO$_2$ is removed from the surface (Figure S3b). On charge to 4.4 V, the NaO$_2$ signal is completely absent, as expected given the complete removal of NaO$_2$ from the electrode surface (Figure S3c). The O1s spectrum at this point is dominated by a C-O signal, and is in agreement with conclusions made in the body of this report that charging to 4.4 V successfully oxidizes all NaO$_2$, but does not oxidize a majority of the carboxylate products. The signal at ~537 eV in all samples arises from residual oxygen moieties on the $^{13}$C carbon support.$^4$
Figure S4. The gas evolution profile monitored by on-line mass spectrometry, following 2M H₃PO₄ injection into an enclosure containing a ¹³C cathode charged to a voltage of 3.0 V after previous discharge to 1.0 mAh (see Table S1). The gases correspond to CO₂ (m/z = 44) and ¹³CO₂ (m/z = 45).
Figure S5. Electrochemical profile (blue curve) together with O$_2$ (black curve) and CO$_2$ (red curve) evolution profiles for a cell charged on the 1$^{st}$ cycle (dotted line) and the 5$^{th}$ cycle (solid line). The 5th charge was obtained after 4 cycles with a charge voltage limitation of 3.0 V and a capacity limitation of 1.0 mAh. The fraction of CO$_2$ and O$_2$ generated beyond 3.0 V is greater for the 5$^{th}$ cycle compared to the 1$^{st}$ cycle due to the respective oxidation of accumulated sodium carboxylates, and NaO$_2$ that could not be oxidized at V < 3.0.
Figure S6. The voltage profile of the metallic metal negative electrode (i.e., counter electrode) in a Na-O_2 cell cycled with a working electrode (^{13}C- carbon) cut-off potential of 3.0 V on charge. The stripping/plating profile shows very little variance from cycle to cycle.
Figure S7. Discharge capacity as a function of cycle number of a $^{13}$C cathode in 0.5M NaOTf/15 ppm H$_2$O/diglyme electrolyte. The cell was operated with a capacity limitation of 0.5 mAh, in a voltage window of 1.8 – 3.0 V. Approximately 20 cycles are reached before capacity fade begins, where a rapid decrease in capacity is observed, that eventually leads to cell death. A post-mortem image of the cathode is shown in the inset.
Figure S8. $^1$H NMR solution spectra of D$_2$O-extracted solid products after exposure of diglyme to chemically generated O$_2^-$ for four days. Each reaction was conducted with 2.5 mL diglyme, 0.02 g KO$_2$, and 0.13 g crown ether (black line). To generate NaO$_2$, 0.1 g of NaOTf was introduced into the solution at the same time as KO$_2$/crown ether addition (red line). The spectral peaks are assigned to sodium acetate (left) and sodium formate (right). Both spectra were normalized to an internal benzene standard.

