SUPPORTING INFORMATION

The role of iodide on the formation of lithium hydroxide in lithium-oxygen batteries

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Figure S1. UV-Vis spectra of diluted stock solutions 0.3 M LiI – black curve, 0.2 M LiI + 0.0025 M I$_2$ – red curve and 0.05 M I$_2$ – blue curve. The spectra show the characteristic absorbance of I$^-$ (223 nm), I$_3^-$ (293 and 365 nm) and I$_2$ (245 nm, 451 nm). The observed peak at 240 nm for solution with I$_2$ is so far unidentified. It could be due to formation of either specific solvent–I$^-$ or solvent–I$^+$ complexes.$^1$
Figure S2 Calibration of I$_3^-$ concentration done by measurement of different dilutions of stock solution 0.2 M LiI + 0.005M I$_2$ in DME a) signal at 364 nm b) signal at 293 nm
Table S1. Calculations of the triiodide concentration and the scale factor for figure plotting.

<table>
<thead>
<tr>
<th>sample</th>
<th>dilute 1</th>
<th>dilute 2</th>
<th>dilute 3</th>
<th>Absorption</th>
<th>$^\wedge C$</th>
<th>#Factor plotted / measured</th>
<th>Titration C$I_3^-$ / mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1M KO$_2$, 0.3 M LiTFSI, 40 ppm H$_2$O, 0.5 h</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.1M KO$_2$, 0.3 M LiTFSI, 1000 ppm H$_2$O, 8 h</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.1M KO$_2$, 0.2 M LiI, 0.1 M LiTFSI, 40 ppm H$_2$O, 0.5 h</td>
<td>100 µl + 3 ml DME</td>
<td>-</td>
<td>-</td>
<td>2.06</td>
<td>1.07</td>
<td>1.20 ± 0.01</td>
<td>0.05</td>
</tr>
<tr>
<td>0.1M KO$_2$, 0.2 M LiI, 0.1 M LiTFSI, 1000 ppm H$_2$O, 8 h</td>
<td>100 µl + 3 ml DME</td>
<td>1 ml + 2 ml DME</td>
<td>0.46</td>
<td>0.24</td>
<td>24.5 ± 0.8</td>
<td>2.1</td>
<td>24.4 ± 0.3</td>
</tr>
<tr>
<td>0.1M KO$_2$, 0.2 M LiI, 0.1 M LiTFSI, 2000 ppm H$_2$O, 8 h</td>
<td>100 µl + 3 ml DME</td>
<td>1 ml + 2 ml DME</td>
<td>0.91</td>
<td>0.47</td>
<td>49 ± 1</td>
<td>2.1</td>
<td>49.3 ± 0.3</td>
</tr>
<tr>
<td>0.1M KO$_2$, 0.2 M LiI, 0.1 M LiTFSI, 3000 ppm H$_2$O, 8 h</td>
<td>100 µl + 3 ml DME</td>
<td>1 ml + 2 ml DME</td>
<td>0.95</td>
<td>0.49</td>
<td>51 ± 2</td>
<td>2.1</td>
<td>50.6 ± 0.3</td>
</tr>
<tr>
<td>0.3 M LiI, 40 ppm H$_2$O, Argon, 1 week</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.3 M LiI, 40 ppm H$_2$O, Oxygen, 1 week</td>
<td>50 µl + 0.55 ml DME</td>
<td>-</td>
<td>-</td>
<td>1.46</td>
<td>0.76</td>
<td>0.312 ± 0.03</td>
<td>0.9</td>
</tr>
<tr>
<td>0.3 M LiI, 1000 ppm H$_2$O, Oxygen, 1 week</td>
<td>100 µl + 1.0 ml DME</td>
<td>100 µl + 1.0 ml DME</td>
<td>0.62</td>
<td>0.32</td>
<td>0.95 ± 0.02</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>0.1M KO$_2$, 0.3 M KI, 40 ppm H$_2$O, 2 days</td>
<td>300 µl + 0.55 ml DME</td>
<td>-</td>
<td>-</td>
<td>&lt;0.01</td>
<td>1</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>0.1M KO$_2$, 0.3 M KI, 1000 ppm H$_2$O, 2 days</td>
<td>100 µl + 0.55 ml DME</td>
<td>-</td>
<td>-</td>
<td>0.13</td>
<td>&lt;0.01</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Li$_2$O$_2$, 0.3 M LiI, 40 ppm H$_2$O, 2 days</td>
<td>10 µl + 0.55 ml DME</td>
<td>-</td>
<td>-</td>
<td>0.70</td>
<td>0.36</td>
<td>0.729 ± 0.007</td>
<td>1</td>
</tr>
<tr>
<td>Li$_2$O$_2$, 0.3 M LiI, 1000 ppm H$_2$O, 2 days</td>
<td>10 µl + 0.55 ml DME</td>
<td>-</td>
<td>-</td>
<td>0.97</td>
<td>0.51</td>
<td>1.03 ± 0.01</td>
<td>1</td>
</tr>
<tr>
<td>Li$_2$O$_2$, 0.3 M LiI, 5000 ppm H$_2$O, 2 days</td>
<td>10 µl + 2.55 ml DME</td>
<td>-</td>
<td>-</td>
<td>0.74</td>
<td>0.38</td>
<td>3.57 ± 0.04</td>
<td>3.6</td>
</tr>
<tr>
<td>Sample Description</td>
<td>Dilute 1</td>
<td>Dilute 2</td>
<td>Dilute 3</td>
<td>Absorption</td>
<td>(\text{^C} I_3^- / \text{mM})</td>
<td>#Factor plotted / measured</td>
<td>Titration C (I_3^-)/mM</td>
</tr>
<tr>
<td>-----------------------------------------------------------------------------------</td>
<td>---------------------------</td>
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<td>---------------------------</td>
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<td>-----------------------------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>0.1M KO(_2), 0.3 M LiTFSI, 40 ppm H(_2)O + 0.2 M LiI, 0.5 h</td>
<td>100 µl + 3 ml DME</td>
<td>-</td>
<td>-</td>
<td>1.05</td>
<td>0.55</td>
<td>0.627 ± 0.006</td>
<td>0.2</td>
</tr>
<tr>
<td>0.1M KO(_2), 0.3 M LiTFSI, 40 ppm H(_2)O + 0.2 M LiI, 16 h</td>
<td>100 µl + 1.55 ml DME</td>
<td>-</td>
<td>-</td>
<td>1.00</td>
<td>0.50</td>
<td>0.311 ± 0.003</td>
<td>-</td>
</tr>
<tr>
<td>0.1M KO(_2), 0.3 M LiTFSI, 1000 ppm H(_2)O + 0.2 M LiI, 24 h</td>
<td>100 µl + 3 ml DME</td>
<td>100 µl + 3 ml DME</td>
<td>-</td>
<td>1.25</td>
<td>0.64</td>
<td>23.0 ± 0.5</td>
<td>1</td>
</tr>
<tr>
<td>0.1M KO(_2), 0.3 M LiI, H(_2)O:LiI = 0.25, H(_2)O:DME = 0.01, 24 h</td>
<td>50 µl + 3 ml DME</td>
<td>100 µl + 1 ml DME</td>
<td>0.5 ml + 3 ml DME</td>
<td>0.70</td>
<td>0.26</td>
<td>44 ± 1</td>
<td>-</td>
</tr>
<tr>
<td>0.1M KO(_2), 0.3 M LiI, H(_2)O:LiI = 0.50, H(_2)O:DME = 0.02, 24 h</td>
<td>50 µl + 3 ml DME</td>
<td>100 µl + 1 ml DME</td>
<td>0.5 ml + 3 ml DME</td>
<td>0.75</td>
<td>0.29</td>
<td>48 ± 1.5</td>
<td>-</td>
</tr>
<tr>
<td>0.1M KO(_2), 0.3 M LiI, H(_2)O:LiI = 1.00, H(_2)O:DME = 0.03, 24 h</td>
<td>50 µl + 3 ml DME</td>
<td>100 µl + 1 ml DME</td>
<td>0.5 ml + 3 ml DME</td>
<td>0.76</td>
<td>0.30</td>
<td>49 ± 1.5</td>
<td>-</td>
</tr>
<tr>
<td>0.1M KO(_2), 0.3 M LiI, H(_2)O:LiI = 2.00, H(_2)O:DME = 0.06, 24 h</td>
<td>50 µl + 3 ml DME</td>
<td>100 µl + 1 ml DME</td>
<td>0.5 ml + 3 ml DME</td>
<td>0.71</td>
<td>0.27</td>
<td>45 ± 1</td>
<td>-</td>
</tr>
<tr>
<td>0.1M KO(_2), 0.3 M LiI, H(_2)O:LiI = 5.00, H(_2)O:DME = 0.16, 24 h</td>
<td>50 µl + 1 ml DME</td>
<td>50 µl + 2.5 ml DME</td>
<td>-</td>
<td>0.80</td>
<td>0.32</td>
<td>12.4 ± 0.2</td>
<td>-</td>
</tr>
<tr>
<td>0.1M KO(_2), 0.3 M LiI, H(_2)O:LiI = 12.0, H(_2)O:DME = 0.40, 24 h</td>
<td>0.5 ml + 2 ml DME</td>
<td>-</td>
<td>-</td>
<td>0.61</td>
<td>0.32</td>
<td>0.06 ± 0.0006</td>
<td>-</td>
</tr>
<tr>
<td>0.1M KO(_2), 0.3 M LiI, H(_2)O:LiI = 24.0, H(_2)O:DME = 0.86, 24 h</td>
<td>1.5 ml + 1 ml DME</td>
<td>-</td>
<td>-</td>
<td>0.03</td>
<td>0.01</td>
<td>&lt;0.0001</td>
<td>-</td>
</tr>
</tbody>
</table>

*Absorptions intensities at \(\lambda_1 = 293\) nm and \(\lambda_2 = 364\) nm. \(^{\text{C}}\) Calculated concentration of \(I_3^-\) from the average of the two absorption bands unless one of the absorbance is out of calibration scale then only one wavelength was used. \(^{\#}\) Factor by which the measured data is scaled in order to visualize the difference in triiodide concentration in the manuscript figures. The \(I_3^-\) concentration error (determined from UV-Vis method) comes mostly from the pipetting procedure that varies depending on the number of dilutions and is estimated to 1%, 2% and 3% for 1, 2 and 3 dilutions, respectively. The \(I_3^-\) concentration error (determined from iodometric titration) is based on the burette tolerance of ±0.05 ml and equal to ±0.3 mM.
Figure S3. a) The LiI concentration dependence of I$_3^-$ concentration after 30 min of reaction. The solutions tested where I) 0.1 M LiI + 0.2 M LiTFSI, II) 0.2 M LiI + 0.1 M LiTFSI, III) 0.3 M LiI and IV) 0.5 M LiI. b) The time dependence of I$_3^-$ concentration in solution where 0.1 M KO$_2$ was directly added to 0.2 M LiI + 0.1 M LiTFSI solution in DME with 40 ppm H$_2$O. In all cases, the data is based on UV-Vis measurements only, as titration of the solutions with such small concentrations results in big errors. Each data point was obtained from separate new experiment.
Figure S4. The time dependence of $I_3^-$ concentration in solution where 0.1M KO$_2$ was directly added to 0.2 M LiI + 0.1 M LiTFSI solution in DME with 1000 ppm H$_2$O. Red squares correspond to values obtained from UV-Vis measurements, while black squares from iodometric titration. In general a good agreement between both techniques is observed. Each data point was obtained from separate new experiment.
Figure S5 H\textsuperscript{1}NMR spectra of liquid phase from Figure 1. The spectra show no evidence for decomposition of DME. Moreover, the signal from H\textsubscript{2}O (at ~4.2 ppm) disappeared after addition of KO\textsubscript{2} for all the samples containing LiI except the one containing 3000 ppm of H\textsubscript{2}O (bright red). This confirms participation of H\textsubscript{2}O in chemical processes during disproportionation reaction and formation of triiodide. For sample with 3000 ppm of H\textsubscript{2}O no further increase of I\textsubscript{3}\textsuperscript{-} was observed that corresponds to presence of unreacted H\textsubscript{2}O and lack of Li\textsubscript{2}O\textsubscript{2} phase. Sample with 1000 ppm H\textsubscript{2}O and only LiTFSI salt (bright blue) showed also strong signal from H\textsubscript{2}O at around 3.5 ppm, indicating lack of its consumption during disproportionation reaction. The shifts of the H\textsubscript{2}O position are explained in the manuscript Figure 4a. The liquid part of sample was placed inside the capillary and closed with the Teflon cap. Next, the capillary was placed inside the NMR tube that contained the deuterated DMSO solvent. In such manner we avoid direct mixing of reference and sample solution, so that we can probe specific interactions between the species in the studied solution.
Figure S6. Reference Raman spectra of pure substances. In case of LiI powder, the spectra was evolving during the data acquisition due to oxidation of I⁻ by red laser. Pure LiI does not reveal any signal in the presented range, on the other hand I₃⁻ has multiple signals as seen on blue spectra.
Figure S7 H\textsuperscript{1}NMR spectra of the solid phase from Figure 1. The spectra show tiny amounts of DME decomposition products HCOO\textsuperscript{-} and CH\textsubscript{3}COO\textsuperscript{-} at 8.5 ppm and 1.9 ppm shifts. The concentration of the decomposition products in the solution for H\textsuperscript{1}NMR analysis was around 0.1-0.2 mM (considering 3mM concentration of DMSO) that corresponds to 0.1-0.2 mM concentration in the reaction solution as the same volumes of the solutions were used. Signal at 4.9 ppm corresponds to H\textsubscript{2}O. 2 Strong signals at 3.4 and 3.6 ppm correspond to residual DME. Signal at 2.7 ppm corresponds to DMSO. Small signals at 3.2 ppm could not be identified, however it probably comes from initial impurities of DME as such signals were present in the pristine solution, Figure S5 black curve. The solid part was first dissolved in D\textsubscript{2}O solution with added known amount of DMSO (3 mM) for quantification purpose. The resulted solution was directly placed in the NMR tube (no capillary).
Detailed description on the possibilities of I\(^{-}\) oxidation

Iodide can be oxidized to triiodide by peroxylike species as hydrogen peroxide\(^2\) or hydroperoxy anion, reactions 1-4\(^3\).

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{I}^- &\rightarrow \text{IO}^- + \text{H}_2\text{O} \quad (1) \\
\text{IO}^- + 2\text{I}^- + \text{H}_2\text{O} &\rightarrow \text{I}_3^- + 2\text{OH}^- \quad (2) \\
\text{HO}_2^- + \text{I}^- &\rightarrow \text{IO}^- + \text{OH}^- \quad (3) \\
\text{IO}^- + 2\text{I}^- + \text{H}_2\text{O} &\rightarrow \text{I}_3^- + 2\text{OH}^- \quad (4)
\end{align*}
\]

In fact, iodide is used as an indicator of \(\text{H}_2\text{O}_2\) due to the high absorption coefficient of triiodide that allows detection of trace \(\text{H}_2\text{O}_2\) \((0.05 \text{ mg/dm}^3)\)\(^2\). Indeed \(\text{H}_2\text{O}_2\) species in absence of iodide where detected by the quantofix stripes at concentration of 2 mg/L. Formation of hydrogen peroxide and its related species can occur in few different reaction paths in Li-air battery:

i) superoxide ion reaction\(^4\)-\(^7\) with water\(^7\) or ether based solvent\(^4\) (proton source), reaction 5-7

\[
\begin{align*}
\text{O}_2^- + \text{H}^+\text{H}_2\text{O or DME} &\rightarrow \text{HOO}^* \quad (5) \\
\text{HOO}^* + \text{O}_2^- &\rightarrow \text{HOO}^- + \text{O}_2 \quad (6) \\
\text{Li}^+ + \text{HOO}^- + \text{H}_2\text{O} &\rightarrow \text{LiOH} + \text{H}_2\text{O}_2 \quad (7)
\end{align*}
\]

ii) lithium peroxide reaction with water\(^7\) or ether based solvent\(^8\)-\(^10\), reaction 8-9

\[
\begin{align*}
\text{Li}_2\text{O}_2 + 2\text{H}_2\text{O} &\leftrightarrow 2\text{LiOH} + \text{H}_2\text{O}_2 \quad (8) \\
\text{Li}_2\text{O}_2 + \text{CH}_3\text{O-R}_1 &\leftrightarrow \text{CH}_3\text{OLi} + \text{R}_2 + \text{HOO}^-\text{Li}^+ \quad (9)
\end{align*}
\]

and iii) \(\text{O}_2\) reaction with ether based solvent, reaction 10-11\(^4\),\(^6\),\(^11\).

\[
\begin{align*}
\text{RH} + \text{O}_2 &\rightarrow \text{R}^* + \text{HOO}^* \quad (10) \\
\text{RH} + \text{HOO}^* &\rightarrow \text{R}^* + \text{H}_2\text{O}_2 \quad (11)
\end{align*}
\]
Figure S8. The influence of oxygen, light, and water on the stability of I⁻ in solution. UV-Vis spectra of 0.3 M LiI solutions in DME and DMSO. The spectra are taken after 1 week of storage in defined conditions.
Figure S9. UV-Vis spectra of DME (bottom) and DMSO (top) solutions containing KO₂ after 2 days. Calculation of the I₃⁻ concentration from absorption values at 293 nm and 364 nm was done after subtraction of the reference DME + KO₂ spectra to avoid contribution from O₂⁻ absorption. Only small fraction of the added KO₂ is soluble in the electrolyte, which is higher for DMSO as compare to DME.
Figure S10 SEM images of a) commercial Li$_2$O$_2$ and b) Li$_2$O$_2$ from disproportionation reaction before (top) and after reaction with Lil (bottom).
Figure S11. The UV-Vis spectra of 0.3 M LiI mixed with commercial Li$_2$O$_2$ powder (0.1 g) in DME with 40, 1000 and 5000 ppm H$_2$O after 2 days. The inset shows optical photographs of the mixture after 5 minutes and 2 days.
Figure S12. The time dependence of $I_3^-$ concentration in solution where 0.2 M KO$_2$ was first added to 0.6 M LiTFSI solution and after 20 min 0.4 M LiI solution was added. The final concentrations of Li salt after mixing the two solutions were 0.3 M LiTFSI and 0.2 M LiI. Both solutions were prepared with DME containing 1000 ppm of H$_2$O. Red squares correspond to values obtained from UV-Vis measurements, while black squares from iodometric titration. In general a good agreement between both techniques is observed. Each data point was obtained from separate new experiment.
Figure S13. The FT-IR spectra of pure DME and 0.3 M LiI solution in DME with different H$_2$O content.
Figure S14. The FT-IR spectra of pure DME and 0.3 M LiI solution in DME with different H₂O content showing the region of water bending vibration.
Figure S15. a) 1H NMR spectra of the pristine electrolytes used to perform disproportionation reaction.
Figure S16  Raman spectra of powders obtained from LiO₂ disproportionation reaction (0.3 M LiI + 0.1 M KO₂, 24 h) in different H₂O:DME ratios (The LiI:H₂O ratio indicated on the right) with reaction time 24 h, the powders were washed 3 times with anhydrous DME before the experiment. The coloring scheme is consistent with Figure 5 a, b.
Figure S17. The UV-Vis of diluted electrolyte (0.1M LiI + 0.2M LiTFSI in DME with 1000 ppm H$_2$O) coming from discharged battery at 2.7 V.