Supplementary Information: Mechanism for Singlet Oxygen Production in Li-Ion and Metal-Air Batteries

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In order to approximate the solvation energies, the results of Kwabi *et. al.*¹ were adopted to create linear fits of the various calculated solvation energies as a function of Gutmann donor number, acceptor number, and a combination of both. In the case of predicting the disociation energy of the reaction $\text{Li}^+ + \text{O}_2^- \longrightarrow \text{LiO}_2$ as proposed previously by Kwabi *et. al.*¹ we us a linear fit of the ΔG as a function of the sum of the predicted solvation energy of O_2^- and Li^+ . For computational ease, the fit was done with respect to the solvation energies predicted by the linear fits in Figure S1 (a) and (b) rather than the solvation energies calculated from first principles.

For the study of the decomposition of Li_2CO_3 , all DFT calculations were performed using the Projector Augmented Wave method implemented in real-space in GPAW.² A minimium grid spacing of h=0.16 Å and a k-point density of greater than 30 Å in each reciprocal



Figure S1: The linear fits for (a) the solvation energy of Li^+ as a function of donor number of the solvant, (b) the solvation energy of O_2^- as a function of acceptor number of the solvent, (c) the solvation energy of $\text{Li}O_2$ as a function of the sum of donor and acceptor number of the solvent, and (d) The dissoctiation energy of $\text{Li}O_2$ into Li^+ and O_2^- as a function of the combined solvation energies of the free ions. All numbers are for dimethoxyethane (DME), dimethylsulfoxide (DMSO), acetonitrile (ACN), and dimethylacetamide (DMA) taken from Kwabi *et. al.* in Reference 1.

space dimension was used. Additionally, the PBE functional was used to treat the exchange correlation potential at the level of the generalize gradient approximation. The 001 surface, which is understood to be the most energetically favourable facet of lithium carbonate was generated and repeated twice for a total of 4 layers of lithium carbonate. The bottom two layers were then fixed during relaxation to simulate the interactions with the bulk lattice constants. The effect of increasing the number of repeating the surface 3 times was studied and the difference in decomposition energies was on the order of 1 meV for the whole slab.

The removal of lithium ions was modeled as an electrochemical step with the potential required to remove the lithium ion equal to $V = -\frac{\Delta G}{F}$ where ΔG is the change in Gibbs energy of the chemical reaction of removing the lithium. Additionally we can model the chemical steps of removing CO₂ or O₂ gas by calculating the change in Gibbs energy of the removal. Unlike the previous computational study which examined the removal of the carbonate CO₃ moiety as a single step, we simulate the removal of the stable gaseous molecule



Figure S2: Lithium carbonate surfaces used showing the side-view (a) and top-view (b) for the 1x1 cell as well as the side-view (c) and top-view (d) for the 2x2 cell



Figure S3: Top view of the decomposition of the lithium carbonate surfaces for the 2x2 cell. The structures seen are the pristine (a), then a Li^+ is removed (b), another Li^+ is removed (c), another Li^+ is removed (d), a Li^+ is removed (e), and another Li^+ is removed (f). This is followed by a chemical removal of CO₂ (g) and another chemical removal of CO₂ (h) to leave a superoxide moiety on the surface.

as separate steps. The chemical removal of CO_3 as a single step is largely unphysical and as the carbonate (CO₃) moiety is not stable and the reaction of carbonate to form CO_2 and O_2 would require two carbonates to be released simultaneously. At every point in the decomposition study, each of these steps was examined and if no chemical step was favorable, the Li removal was accepted. The predicted onset potential for the reaction was 4.53 V, which is slightly above the experimentally measured onset potential. This error however is within the error for DFT predictions of electrochemical potentials. To investigate finite size effects on the prediction results, two surface sizes were used as can be seen if Figure S2. The resulting surface after each of the decomposition steps on the 2x2 surface can be seen in Fig S3 and the free energy diagrams for both surface sizes can be seen in Figure S4.



Figure S4: The energy diagram for the decomposition reactions for (a) a 1x1 surface at U=4.77 V and (b) a 2x2 repeated surface at U=4.60 V

For completeness, we also show the schematic for the formation of singlet oxygen during charging of a Na-air battery in Figure S5 as was show in Figure 4 of the main text. It is illustrated, just as in the Li-air case, that the NaO₂ surface releases a NaO₂ into solution which dissociated into Na⁺ and O₂⁻. The disproportionation reaction discussed within the main text occurs, and the resulting Na₂O₂ that is produced will be immediately decomposed into two Na⁺ and O₂⁻ again (accompanied by a single electron transfer) once it precipitates onto the NaO₂ surface.



Figure S5: Schematic of proposed singlet oxygen formation within NaO_2 during charging. For simplicity, we only show the free superoxide anion with a dissociated Na^+ dissolved in solution as this is the predominate mechanism of singlet oxygen production.

References

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