Supplementary Information

The Effect of Water on Discharge Product Growth and Chemistry in Li-O₂ Batteries

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Table S1. Computed solvation energies of water in DME, MeCN, DMF and DMA. Values are reported in kJ/mol.

	Method/basis set			
Solvent	B3LYP/6-31G(d,p)	M06L/6-311++G(d,p)//	CCSD/aug-cc-pVTZ	
		B3LYP/6-31G(d,p)		
DME	12.71	16.46	11.92	
MeCN	18.06	19.79	17.07	
DMF	18.09	19.83	17.11	
DMA	18.10	19.84	17.12	

Table S2. Proton solvation energies in a range of organic solvents and the solvents' dielectric constants.

Solvent	$\Delta G_{s}(H^{+}), kJ/mol$	3
DMSO	-1143.451	46.7
MeCN	-1088.68 ¹	36.64
MeOH	-1061.06 ¹	32.63
EtOH	-1015.79	24.85
Benzene	-882.49	2.271
Acetone	-1032.25	20.49



Figure S1. (a) Current transient responses to potentiostatic discharge at 2.6 V in 0.1M LiClO₄ in DME with < 30 and 5000 ppm of water (first 50,000 seconds of discharge shown). SEM images of potentiostatically discharged electrodes in 0.1M in LiClO₄ in DME with (b) < 30 ppm and (c) 5000 ppm of water. Both samples were discharged to ~0.055 mAh.



Figure S2. XRD pattern of Li-O₂ carbon paper electrode discharged at 2.0 V in 0.1M LiClO₄ in DME with 5000 ppm of water.



Figure S3. Current transient responses (in blue) at a glassy carbon disk electrode held potentiostatically at 2.0, 2.4 and 2.6 V vs Li⁺/Li in O₂-saturated 0.1M LiClO₄ in DME, compared to ideal Cottrell behavior for 1 and 2e⁻ reduction (in black).

Discussion of Figure S3.

Three-electrode cell measurements of oxygen reduction were performed using a glassy carbon working electrode, Li metal counter and reference electrodes, and O_2 -saturated 0.1M LiClO₄ in DME (more details of the three-electrode setup have been described previously²). The current transient obtained at the lowest potential (highest overpotential) of 2.0 V are well below the diffusion-limited currents for both 1 and 2e⁻ O₂ reduction, as dictated by the Cottrell equation:³

$$i = \frac{nFAD^{1/2}C_o}{\pi^{1/2}t^{1/2}},$$
 where n is the number of electrons transferred, F is Faraday's constant, D and C_o are the diffusivity and concentration of oxygen in DME⁴ respectively and t is time. Diffusion-limited Li₂O₂ growth is thus unlikely.



Figure S4. XRD patterns of Li-O₂ CNT electrodes discharged at 25 mA/g_C in 0.1M LiClO₄ in DME with < 30 ppm and 5000 ppm of water.

Calculation of water addition to electrolyte through cell leakage

As noted in the main manuscript, all Li-O₂ cells were pressurized to 25 psi gage, and were noted to have a leak rate of ~ 0.5 psi/day. This translates to a molar loss that can be calculated with the ideal gas equation:

$$\frac{dN}{dt} = \frac{\frac{dP}{dt}V}{RT}$$

where dN/dt is the molar rate of gas loss, dP/dt is the pressure loss, V is internal cell volume, and R and T are the molar gas constant and temperature respectively. For an internal cell volume of 3.5 ml at room temperature, this results in 3.38 nmole/min.

Assuming that water from ambient air leaks into the cell at a similar rate, we can calculate the rate of water addition to the electrolyte. The saturated vapor pressure of water at 25 °C and 1 atm is 0.023 bar. For a relative humidity of 50%, this results in a mole fraction of water in air

 $=\frac{RH \times 0.023 \ bar}{total \ pressure} = 0.011.$ Thus, the number of moles of water per minute is

 $0.011 \times 3.38 \text{ nmole/min} = 0.038 \frac{\text{nmole}}{\text{min}}$. The mass of water added after 160 h is

$$0.038 nmole/\min \times 18 \frac{g}{mol} \times 160 h = 6.64 \mu g$$

In contrast, the mass of water required for a 5000 ppm water concentration is 5000 ppm × 200 μ l of dimethoxyethane × 0.867 g/cm³ = 867 μ g, which is two orders of magnitude greater than the estimated amount added.

It is important to note that although this calculation does not consider water ingress by diffusion through the Teflon spacers of the air cell, the actual amount of water in the electrolyte would be much less than the value calculated here, mainly because (i) the real rate of water entry will be much less than the rate of gas leakage from the cell, due to the adverse pressure differential and (ii) not all the water that enters the cell in vapor phase will dissolve in the electrolyte, i.e. some of it will remain in the gas phase, in equilibrium with solvated water.

Calculation of theoretical CNT discharge capacity assuming void volume filling

CNT electrodes used in this study averaged 1 cm \times 1 cm \times 500 μ m = 0.03 cm³ and 500 μ g in mass. Assuming 60% of the volume of the electrode was available for Li₂O₂ filling (given a void volume of 90%, and the rest occupied by electrolyte) would result in a charge per electrode of

$$Q = \frac{2.36 \frac{g}{cm3} \times 0.03 \ cm3 \ \times 0.6 \times 2 \ \times 96485 \ C/mol}{46 \ g/mol} = 50 \ mAh$$

For an electrode mass of 500 μ g, this results in a discharge capacity of 100, 000 mAh/g_C.



Figure S5. Schematic illustrating competition between surface and solvent-mediated nucleation of Li_2O_2 in the presence of water, which is modulated by electrode surface site concentration and activity. In the presence of water, high concentration and activity of surface sites in CNTs results in greater surface-mediated nucleation, while lower concentration and activity of surface sites in carbon paper results in more solvent-mediated Li_2O_2 nucleation.



Figure S6. Raman spectra of pristine CNT and carbon paper electrodes, showing D and G bands from carbon.



Figure S7. First discharge capacity as a function of current density and water content in the catholyte of cells with carbon paper (squares), Vulcan carbon/Super P (circles) and CNT (diamond)-based electrodes and glyme-based solvents, with assumed specific surface areas of 1, 100 and 500 m²/g respectively. A similar plot is reported in the study by Schwenke *et al.*⁵ with the data of Adams *et al.*⁶ Data from Meini,⁷ Lau,⁸ Aetukuri⁹ and co-workers have been added for comparison.



Figure S8. Thermodynamic cycle showing calculation of pKa of water in different aprotic solvents.



Figure S9. The proton solvation energy, $\Delta G_s(H^+)$, in organic solvents plotted against the solvents' dielectric constants.



Figure S10. Current transients fitted with models for 2-dimensional growth and instantaneous or progressive nucleation for a carbon paper electrode discharged at 2.0 V in 0.1 M LiClO₄ DME with (a) <30 ppm H₂O and (b) 5000 ppm H₂O. (c) Current transient in (b) adjusted so that the local minimum represents the point of zero current and capacity.

Discussion of Figure S10

The equations used for fitting the transients in Figure 1a were $I/I_m = t^2/t_m^2 \exp[-2/3*(t^3/t_m^3 - 1)]$ for progressive nucleation and 2D growth and $I/I_m = t/t_m \exp[-2/3*(t^2/t_m^2 - 1)]$ for instantaneous nucleation and 2D growth, where I and t are current and time, and I_m and t_m are the maximum current and the time it occurs in the peak, respectively.^{10,11,12} These fits can roughly describe the transients in the vicinity of the current peaks but fail to account for the slow current decay at long times (**Figures S10**a-b). We hypothesize that the experimental data is a composite of currents

related to solvent and surface-mediated processes. Solvent-mediated processes would be expected to generate a slowly monotonic decaying current, as solvated Li⁺-O₂⁻ disproportionates and aggregates in solution,^{2,13} before precipitating on and passivating the surface. Current related to direct surface-mediated growth of Li₂O₂ on the other hand, creates a peak and sharp current decay, as predicted by electrodeposition models of nucleation and growth. Since the solvent-mediated current was not incorporated, the analysis overestimates the magnitude of the surface mediated current peak and it is not possible to unambiguously distinguish between behavior typical of an Avrami exponent of n=2 (instantaneous nucleation with 2-D growth) or n=3 (constant progressive nucleation with 2-D growth), which both roughly fit the peak shape. In order to try to determine which behavior was present, the peak was isolated by considering capacity and current to be zero at the local minimum in the current transient before the peak and considering the total capacity to be reached when the current returned to this value after the peak. The analysis assumes that there is a constant current due to a solution mediated process that does not contribute to the peak and is not included in the fractional capacity calculation. This assumption follows from positing that changes in the surface mediated current dominate over changes in the solvent mediated current in the time regime under the peak in total current. The plot in Figure S10c based on fractional capacity in 5000 ppm H₂O allows an estimate of n by fitting the slope of the line, as seen in Figure 1b. This preliminary result that $n\sim2$ suggests that either the nucleation rate or the growth rate decays with time. For a constant growth rate, a value of n=2 suggests that the nucleation rate decreased rapidly with time, such that all nucleation events were essentially simultaneous. Analogous analysis is not shown for the anhydrous DME case as the peak occurred in an earlier time regime where the assumption of a relatively constant solution current is not reasonable. The assumption is invalid because the amplitude of the peak is small relative to the total current. This

can be seen in **Figure S10**a where a fit was produced based on I_m and t_m for n=2 and n=3; the modeled current transients only fit the raw data in a small time regime. Further efforts will be needed to refine this analysis to properly fit the contribution of solution-mediated current in order to make rigorous statements about the nature of surface-based nucleation and growth.

References

- Kelly, C. P.; Cramer, C. J.; Truhlar, D. G. Single-Ion Solvation Free Energies and the Normal Hydrogen Electrode Potential in Methanol, Acetonitrile, and Dimethyl Sulfoxide. *J. Phys. Chem. B* 2007, *111* (2), 408–422.
- Kwabi, D. G.; Tulodziecki, M.; Pour, N.; Itkis, D. M.; Thompson, C. V; Shao-Horn, Y.
 Controlling Solution-Mediated Reaction Mechanisms of Oxygen Reduction Using
 Potential and Solvent for Aprotic Lithium-Oxygen Batteries. *J. Phys. Chem. Lett.* 2016.
- Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications,* 2nd Edition, 2nd ed.; Wiley: New York, 2000.
- (4) Lu, Y.-C.; Kwabi, D. G.; Yao, K. P. C.; Harding, J. R.; Zhou, J.; Zuin, L.; Shao-Horn, Y. The Discharge Rate Capability of Rechargeable Li–O2 Batteries. *Energy Environ. Sci.* 2011, 2999–3007.
- (5) Schwenke, K. U.; Metzger, M.; Restle, T.; Piana, M.; Gasteiger, H. A. The Influence of Water and Protons on Li2O2 Crystal Growth in Aprotic Li-O2 Cells. *J. Electrochem. Soc.* 2015, *162* (4), A573–A584.
- (6) Nazar, L.; Adams, B.; Black, R.; Radtke, C.; Zaghib, K.; Trudeau, M. Current Density

Dependence of Peroxide Formation in the Li-O2 Battery and Its Effect on Charge. *Energy Environ. Sci.* **2013**, *6*, 1772–1778.

- (7) Meini, S.; Piana, M.; Tsiouvaras, N.; Garsuch, A.; Gasteiger, H. A. The Effect of Water on the Discharge Capacity of a Non-Catalyzed Carbon Cathode for Li-O2 Batteries. *Electrochem. Solid-State Lett.* **2012**, *15* (4), A45.
- Lau, S.; Archer, L. A. Nucleation and Growth of Lithium Peroxide in the Li-O2 Battery.
 Nano Lett. 2015, *15* (9), 5995–6002.
- Aetukuri, N. B.; McCloskey, B. D.; García, J. M.; Krupp, L. E.; Viswanathan, V.; Luntz,
 A. C. Solvating Additives Drive Solution-Mediated Electrochemistry and Enhance Toroid
 Growth in Non-Aqueous Li–O2 Batteries. *Nat. Chem.* 2014, 7 (1), 50–56.
- (10) Gerber, L. C. H.; Frischmann, P. D.; Fan, F. Y.; Doris, S. E.; Qu, X.; Scheuermann, A. M.; Persson, K.; Chiang, Y.-M.; Helms, B. A. Three-Dimensional Growth of Li2S in Lithium-Sulfur Batteries Promoted by a Redox Mediator. *Nano Lett.* 2016, *16* (1), 549–554.
- (11) Bewick, A.; Fleischmann, M.; Thirsk, H. R. Kinetics of the Electrocrystallization of Thin Films of Calomel. *Trans. Faraday Soc.* **1962**, *58*, 2200.
- (12) Fleischmann, M.; Thirsk, H. R. Electrochemical Kinetics of Formation of Monolayers of Solid Phases. *Electrochim. Acta* 1964, 9 (6), 757–771.
- (13) Zakharchenko, T. K.; Kozmenkova, A. Y.; Itkis, D. M.; Goodilin, E. A. Lithium Peroxide Crystal Clusters as a Natural Growth Feature of Discharge Products in Li-O2 Cells. *Beilstein J. Nanotechnol.* 2013, *4*, 758–762.