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Supporting Information

Deciphering the role of LiBr as redox mediator in Li-O_2 Aprotic Batteries

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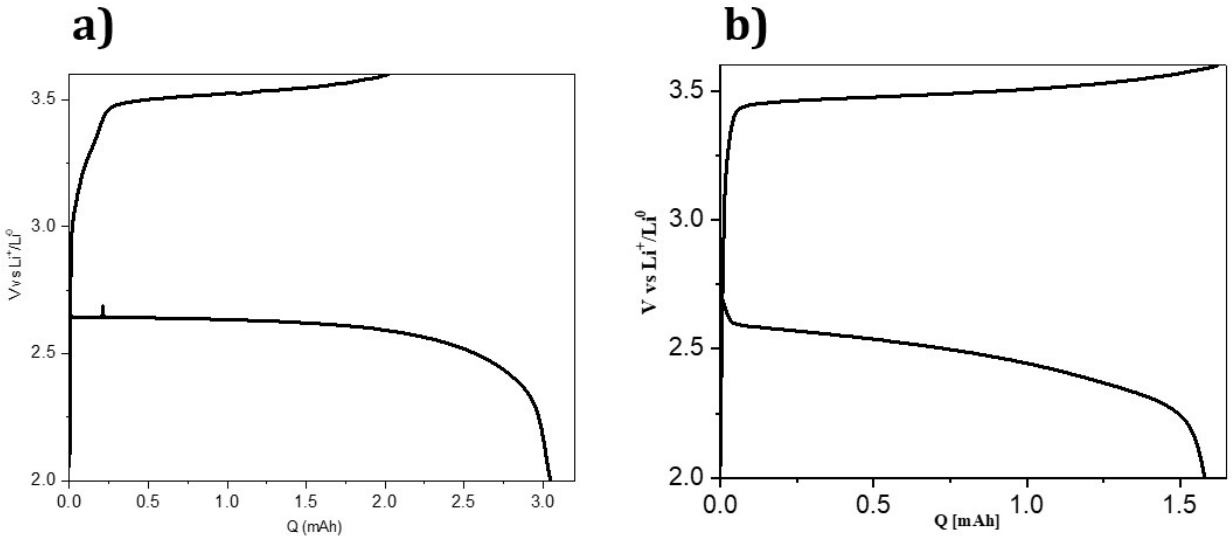


Figure S1: *Discharge/charge profiles of a Li-O_2 cell cycled at 0.1 mA/cm² between 2.0 and 3.6 V vs. Li^+/Li^0, with no capacity limit, using a) LiTFSI 1M + LiBr 100 mM in DME electrolyte (1 bar of pre-loaded O_2) and b) LiTFSI 1M + LiBr 200 mM in DME electrolyte (0.8 bar of pre-loaded O_2). N.B. The capacity difference is owed to a different pre-loading of O_2 in the cell headspace.*

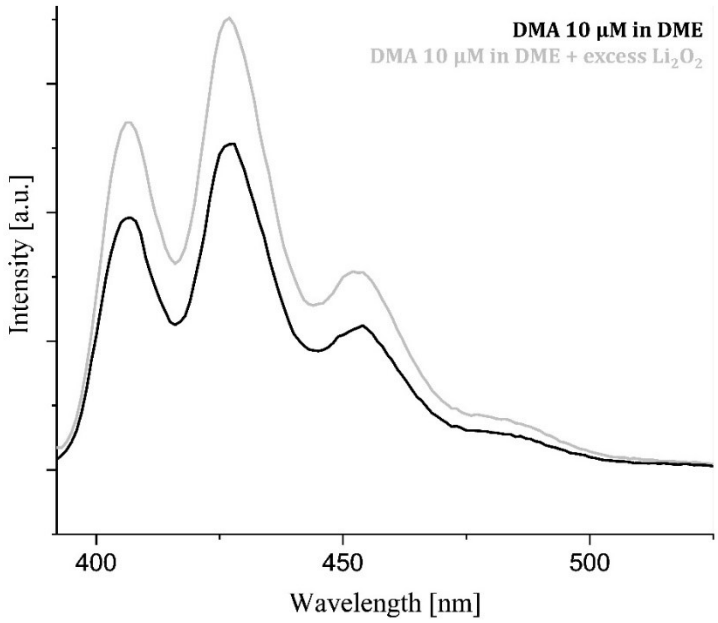


Figure S2: *Fluorescence spectra of a solution of DMA 10µM in DME before (black) and after (grey) adding excess Li_2O_2.*

Table S1: *Integration of DMA signals and corresponding values of intensity increase upon adding Li_2O_2.*

	Sample (in DME)	Signal integral [a.u]	DMA Fluorescence increase after adding Li_2O_2
Figure 2b	DMA 10µM + $LiBr_3$ 10µM + excess Li_2O_2	2160	40,1%
	DMA 10µM + $LiBr_3$ 10µM	1542	
Figure S1	DMA 10µM + excess Li_2O_2	3025	40,2%
	DMA 10µM	2157	

Boltzmann distribution of states. The amount of release of $^1O_2$ during ORR in absence of other preferential reaction routes is determined by the Boltzmann factor. Being the difference in energy between the triplet and singlet states of molecular oxygen 0.97 eV[1], the ratio $P(^1O_2)/P(^3O_2)$ at room temperature can be calculated according to Eq. S1.

Equation S1

$$\frac{P(^1O_2)}{P(^3O_2)} = e^{\frac{\Delta E}{k_B t}} = 3.939 \cdot 10^{-17}$$

Thus, the probability associated to the formation of $^1O_2$ is almost negligible in this case.

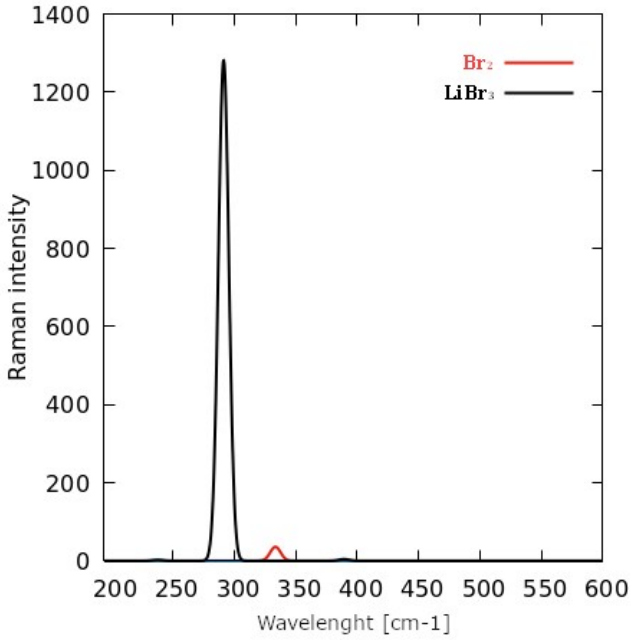
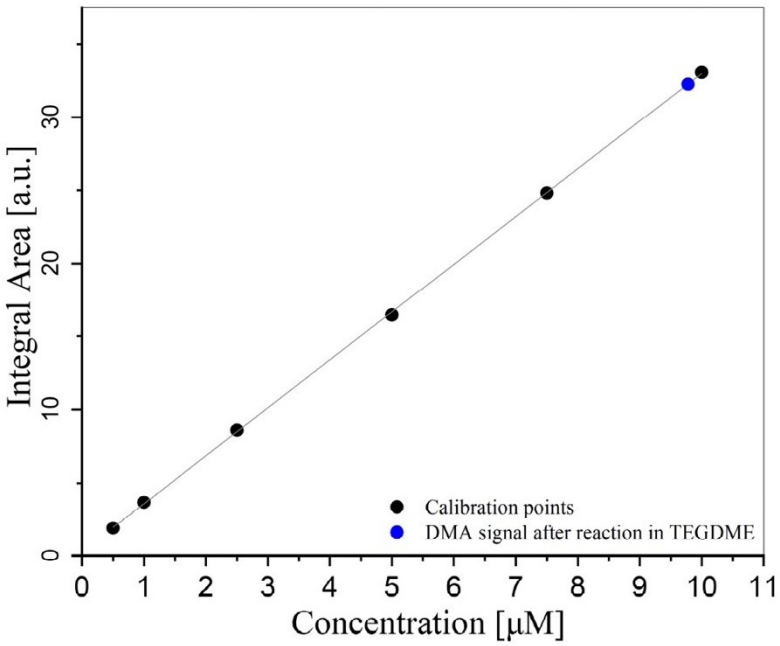


Figure S3: *Simulation of $LiBr_3$ and Br_2 Raman signals.*



Fitting parameters

Equation	y = a + b*x
Plot	integral
Weight	No Weighting
Intercept	0.3126 ± 0.09212
Slope	3.26964 ± 0.01643
Residual Sum of Squares	0.07738
Pearson's r	0.99995
R-Square (COD)	0.9999
Adj. R-Square	0.99987

Figure S4. *Calibration line and corresponding fitting parameters for accurate calculation of DMA concentration after the oxidation of Li_2O_2 by Br_3^- in TEGDME (blue dot).*

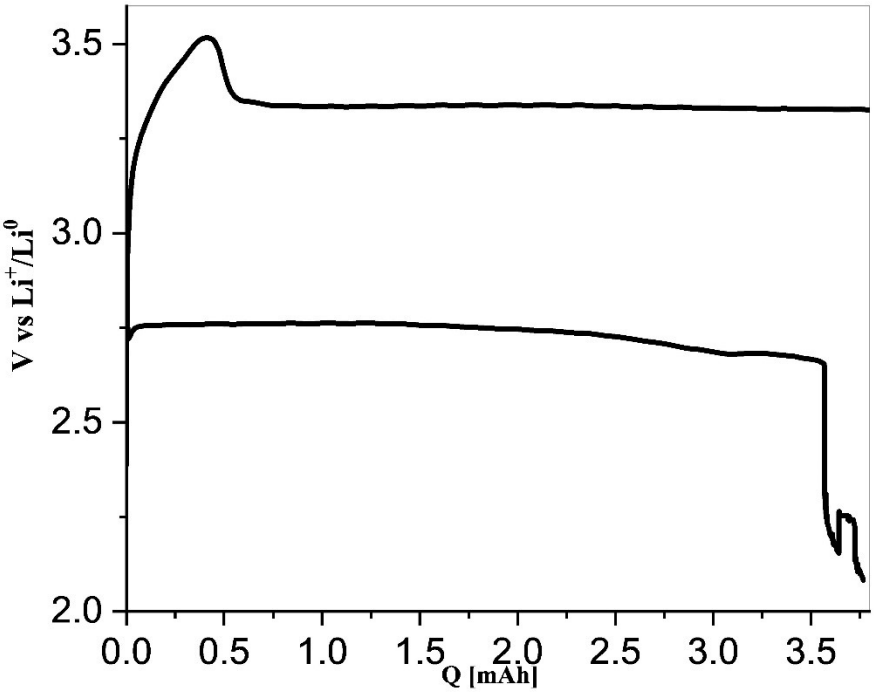


Figure S5. *Discharge/charge profiles of a Li-O_2 cell cycled at 0.1 mA/cm^2 between 2.0 and 3.6 V vs. Li^+/Li^0, with no capacity limit, using a LiTFSI 1M + LiBr 200 mM in DMSO electrolyte.*

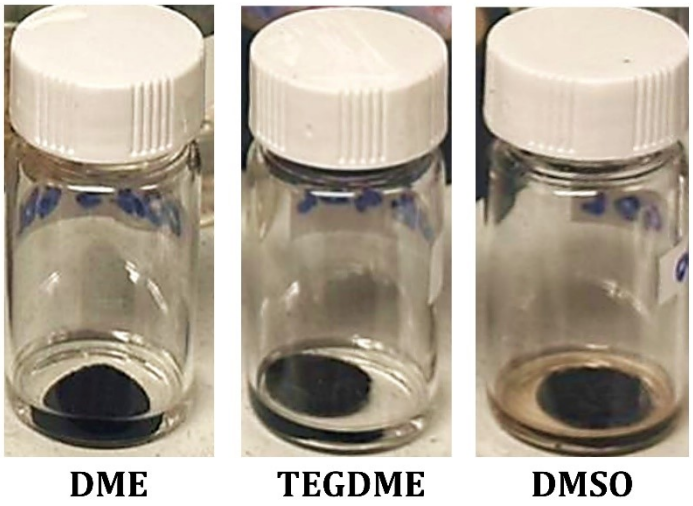


Figure S6*. Pictures of GDL cathodes washed with fresh solvent and recovered after the cycling procedures for each electrolyte formulation.*

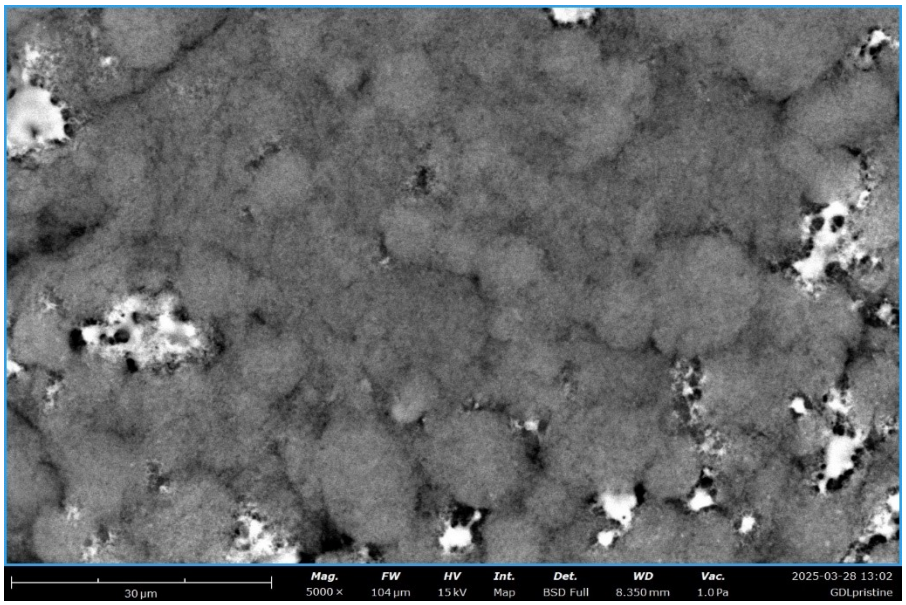


Figure S7. *Scanning Electron Microscopy image (5.000x magnification, working distance of 8.35 mm, 15kV electron beam energy) of the pristine Gas Diffusion Layer cathode.*

Table S2. *EDX elemental quantitative analysis of the pristine Gas Diffusion Layer.*

Sample	Atomic %			
	C	O	S	F
$GDL_{(Pristine)}$	84.07	1.8	0.2	13.8

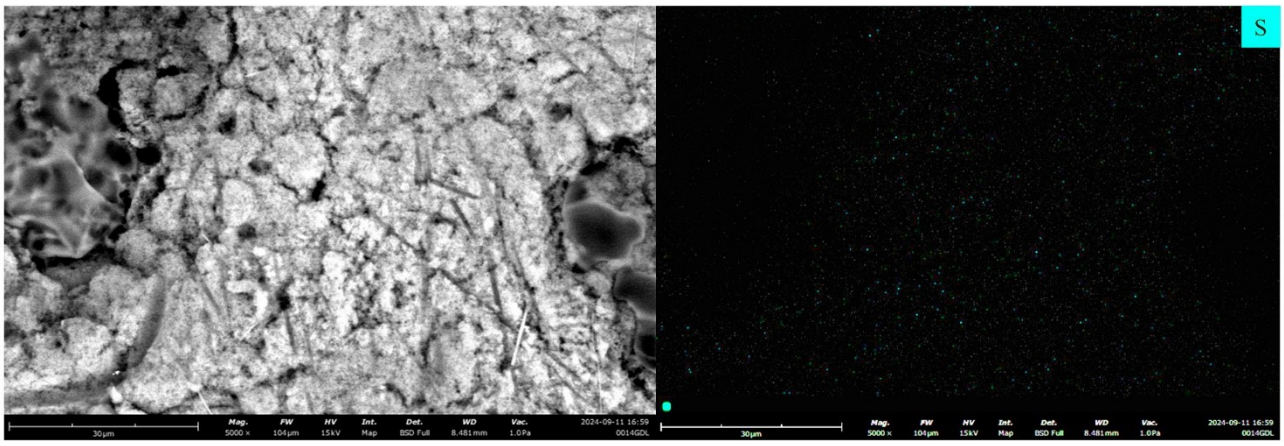


Figure S8. *SEM image (5.000x magnification, 15kV electron beam energy, working distance 8.48 mm) of cycled* $GDL_{(TEGDME)}$ *and corresponding EDX elemental mapping of Sulfur.*

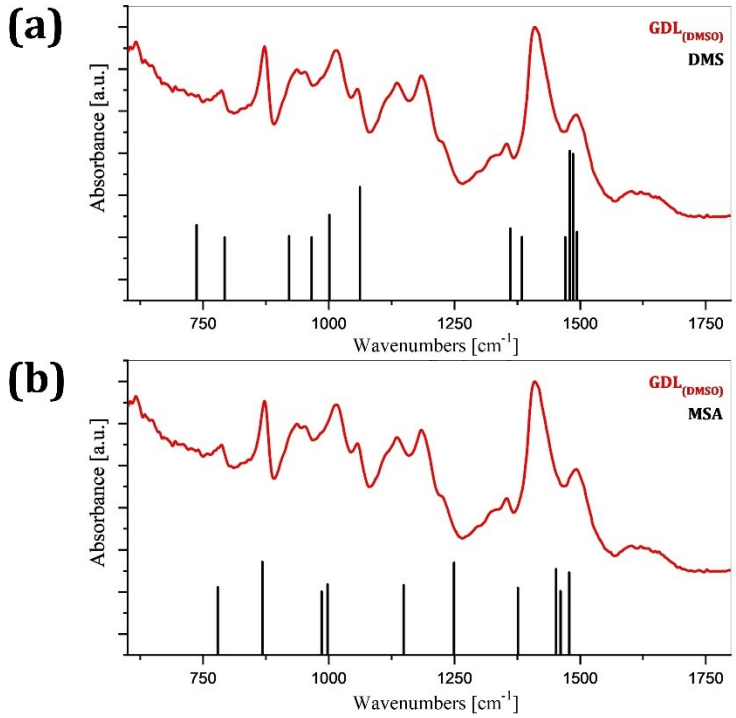


Figure S9. *Comparison between $GDL_{(DMSO)}$ spectrum and theoretical FTIR signals of (a) dimethyl sulfide (DMS) and (b) methanesulfonic acid (MSA).*

References

1. Hong, Y. S. *et al.* Safe Lithium-Metal Anodes for Li-O_2 Batteries: From Fundamental Chemistry to Advanced Characterization and Effective Protection. *Batter. Supercaps* **2**, 638–658 (2019).