Supporting Information: Understanding the Fundamentals of Redox Mediators in Li-O_2 Batteries: A Case Study on Nitroxides

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Fig. S1a) SEM image of the porous separator (Whatman GF/A) after sputter coating with platinum, obtained with a Merlin high-resolution Schottky field-emission microscope (Zeiss SMT); b) Cyclic voltammogram of 100 mM TEMPO in 1 M LiTFSI/diglyme under argon atmosphere (p = 1 bar); obtained in a setup according to Fig. 1 with a scan speed of 5 mV s⁻¹.

Fig. S2a) Potentiostatic measurements of 100 mM TEMPO in 1 M LiTFSI/diglyme using a) different interelectrode distances d and a fixed cathodic potential E = 3.95 V vs. Li⁺/Li or b) different cathodic potentials E and a fixed interelectrode distance d = 200 µm; all data were obtained with a GC working electrode, a LFP counter electrode and a lithium reference electrode, compare Fig. 1.
**Fig. S3** Cyclic voltammograms of 10 mM a) TEMPO 4, b) 4-methoxy-TEMPO 5, c) AZADO 6, d) TMAO 8 in 1 M LiTFSI/diglyme using different scan speeds; obtained in a glass cell according to 2.3 under argon atmosphere ($p = 1$ bar).

**Fig. S4** Cyclic voltammograms of 10 mM a) TEMPO 4, b) 4-methoxy-TEMPO 5, c) AZADO 6, d) TMAO 8 in 1 M LiTFSI/diglyme under argon and oxygen atmosphere ($p = 1$ bar); obtained in a glass cell according to 2.3 with a scan speed of 50 mV s$^{-1}$. 
Fig. S5 Cycling profiles of Li-O₂ cells with 1 M LiTFSI/diglyme using $j = 0.1 \text{ mA cm}^{-2}$, $p(O_2) = 1 \text{ bar}$ and a) a fixed discharge capacity of 1000 mAh g$^{-1}$ or b) a fixed discharge cut-off voltage of 2.0 V; a section up to 4.2 V was selected according to the residual Li-O₂ cells with nitroxides, see Fig. S7.

Fig. S6 Cycling profiles of Li-O₂ cells with 10 mM a) TEMPO 4, b) 4-methoxy-TEMPO 5, c) TMAO 8 in 1 M LiTFSI/diglyme; obtained with $j = 0.1 \text{ mA cm}^{-2}$, $p(O_2) = 1 \text{bar}$ and cut-off potentials of 2.0 V resp. 4.2 V vs. Li$^+$/Li. The corresponding profile of a Li-O₂ cell with pure 1 M LiTFSI/diglyme is shown in Fig S5b.
Fig. S7 Cycling profiles of Li-O₂ cells with 10 mM and 100 mM TEMPO in 1 M LiTFSI/diglyme using $j = 0.1$ mA cm$^{-2}$, $p(O_2) = 1$ bar and a fixed discharge capacity of 1000 mAh g$^{-1}$.

Fig. S8 XRD patterns of the carbon cathodes after discharge and charge in a Li-O₂ cell with 10 mM a) TEMPO 4, b) 4-methoxy-TEMPO 5, c) TMAO 8 in 1 M LiTFSI/diglyme; the corresponding cycling profiles are illustrated in Fig. S6. Li₂O₂ diffraction pattern matches the typical Li₂O₂ faces (ICSD 98-018-0557).