Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

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

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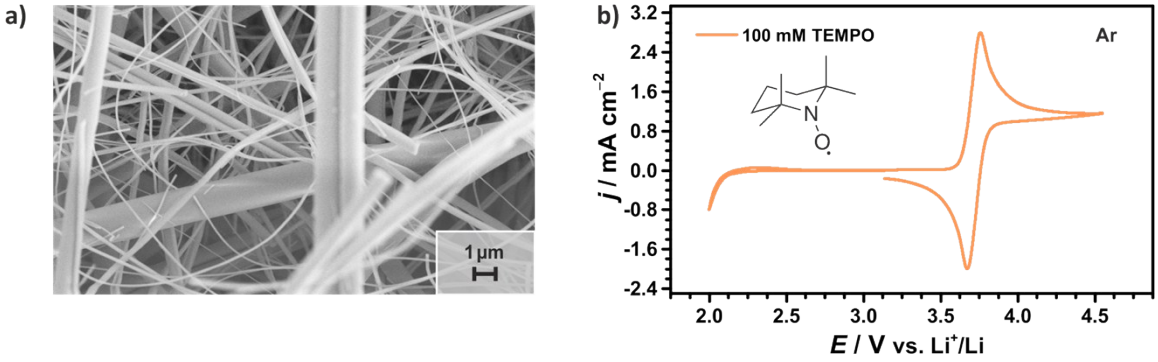

Fig. S1a) SEM image of the porous separator (Whatman GF/A) after sputter coating with platinum, obtained with a Merlin high-resolution Schottky field-emission microscope (Zeiss SMT); **b)** Cyclic voltammogram of 100 mM TEMPO in 1 M LiTFSI/diglyme under argon atmosphere (p = 1 bar); obtained in a setup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

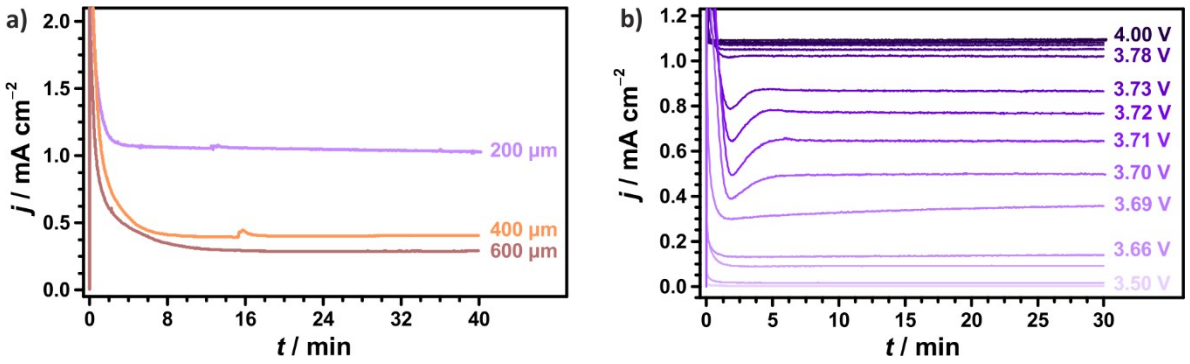

Fig. S2a) Potentiostatic measurements of 100 mM TEMPO in 1 M LiTFSI/diglyme using **a)** different interelectrode distances d and a fixed cathodic potential E = 3.95 V vs. Li^+/Li or **b)** different cathodic potentials E and a fixed interelectrode distance d = 200 µm; all data were obtained with a GC working electrode, a LFP counter electrode and a lithium reference electrode, compare Fig. 1.

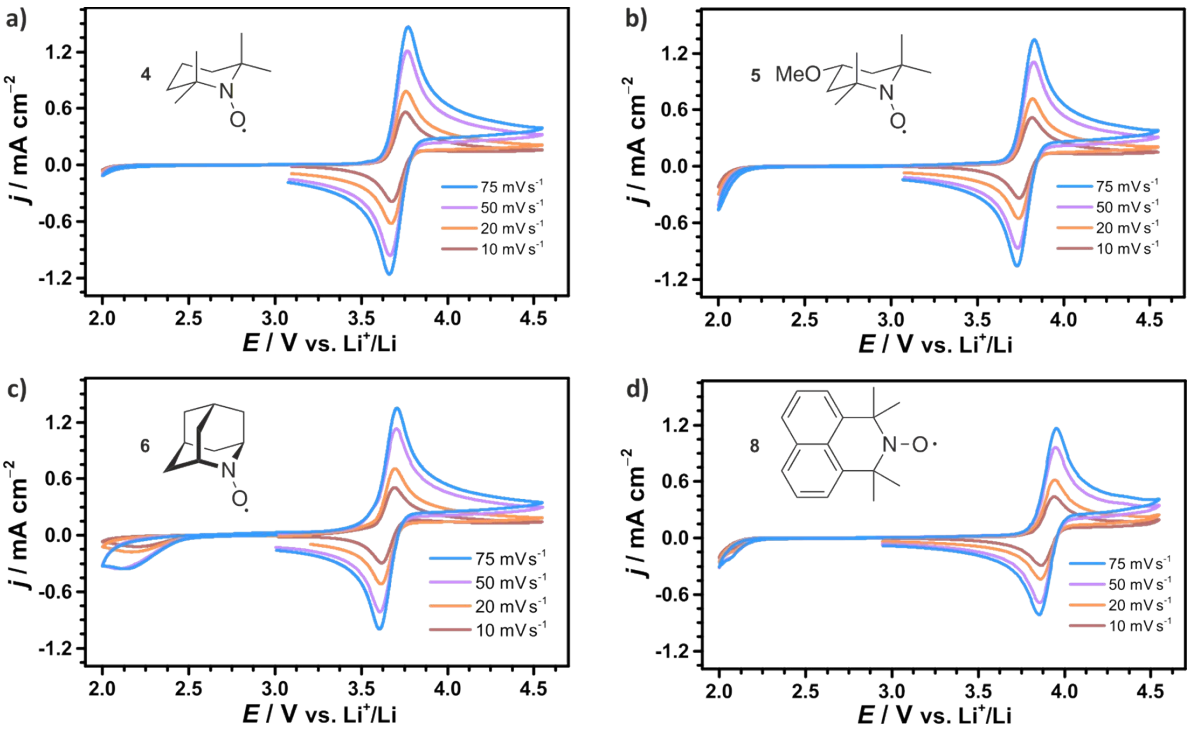

Fig. S3 Cyclic voltammograms of 10 mM **a)** TEMPO **4**, **b)** 4-methoxy-TEMPO **5**, **c)** AZADO **6**, **d)** TMAO **8** in 1 M LiTFSI/diglyme using different scan speeds; obtained in a glass cell according to 2.3 under argon atmosphere (p = 1 bar).

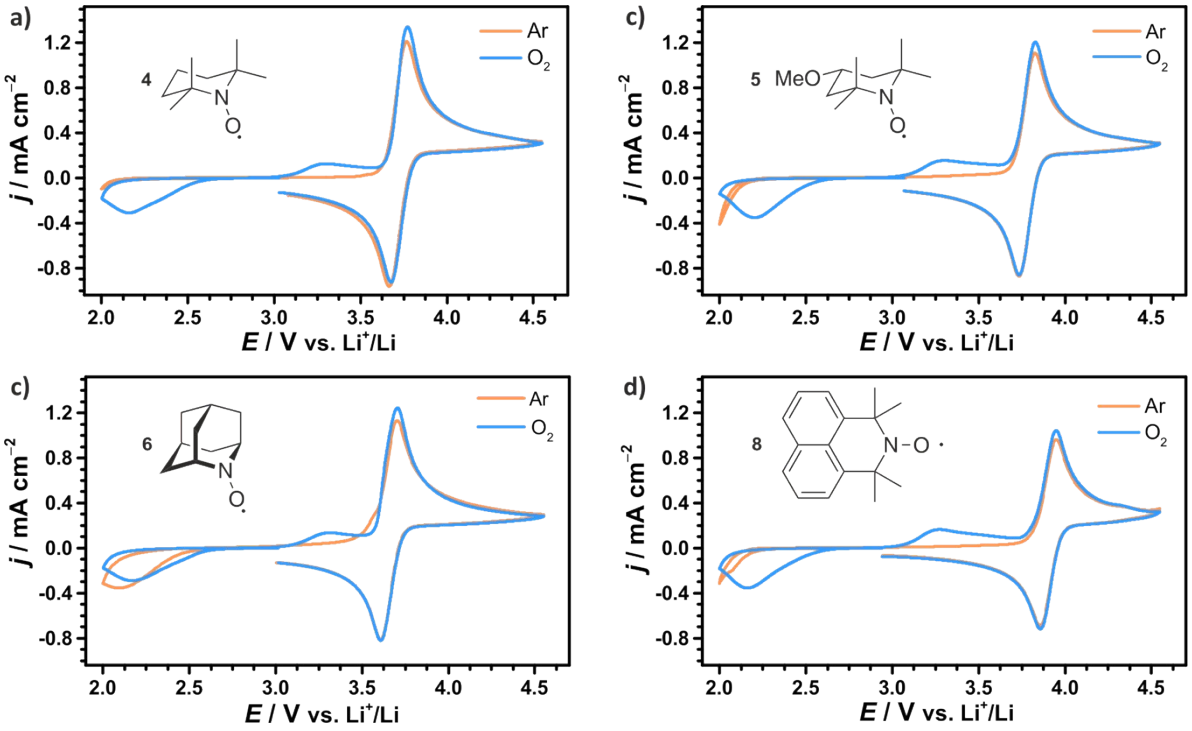

Fig. S4 Cyclic voltammograms of 10 mM **a)** TEMPO **4**, **b)** 4-methoxy-TEMPO **5**, **c)** AZADO **6**, **d)** TMAO **8** in 1 M LiTFSI/diglyme under argon and oxygen atmosphere (p = 1 bar); obtained in a glass cell according to 2.3 with a scan speed of 50 mV s^{-1}.

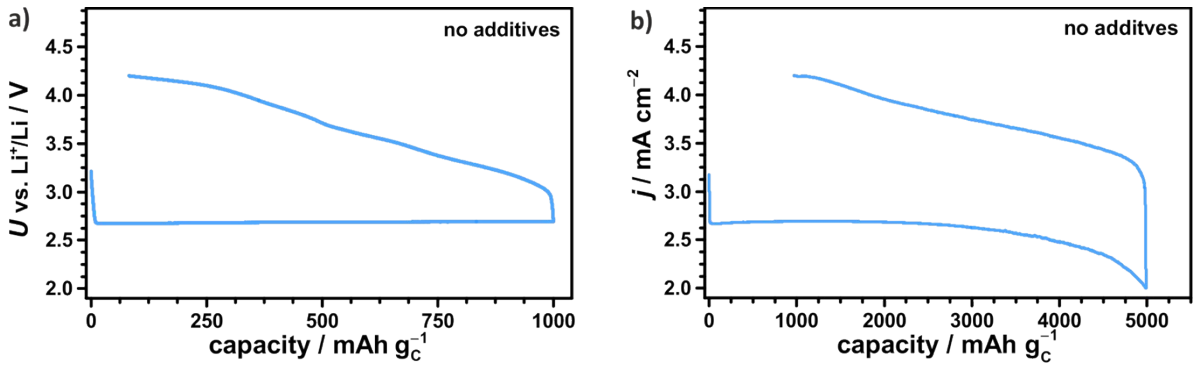

Fig. S5 Cycling profiles of Li-O_2 cells with 1 M LiTFSI/diglyme using j = 0.1 mA cm^{-2}, $p(O_2)$ = 1 bar and **a)** a fixed discharge capacity of $1000\ \mathrm{mAh\ g_C^{-1}}$ or **b)** a fixed discharge cut-off voltage of 2.0 V; a section up to 4.2 V was selected according to the residual Li-O_2 cells with nitroxides, see Fig. S7.

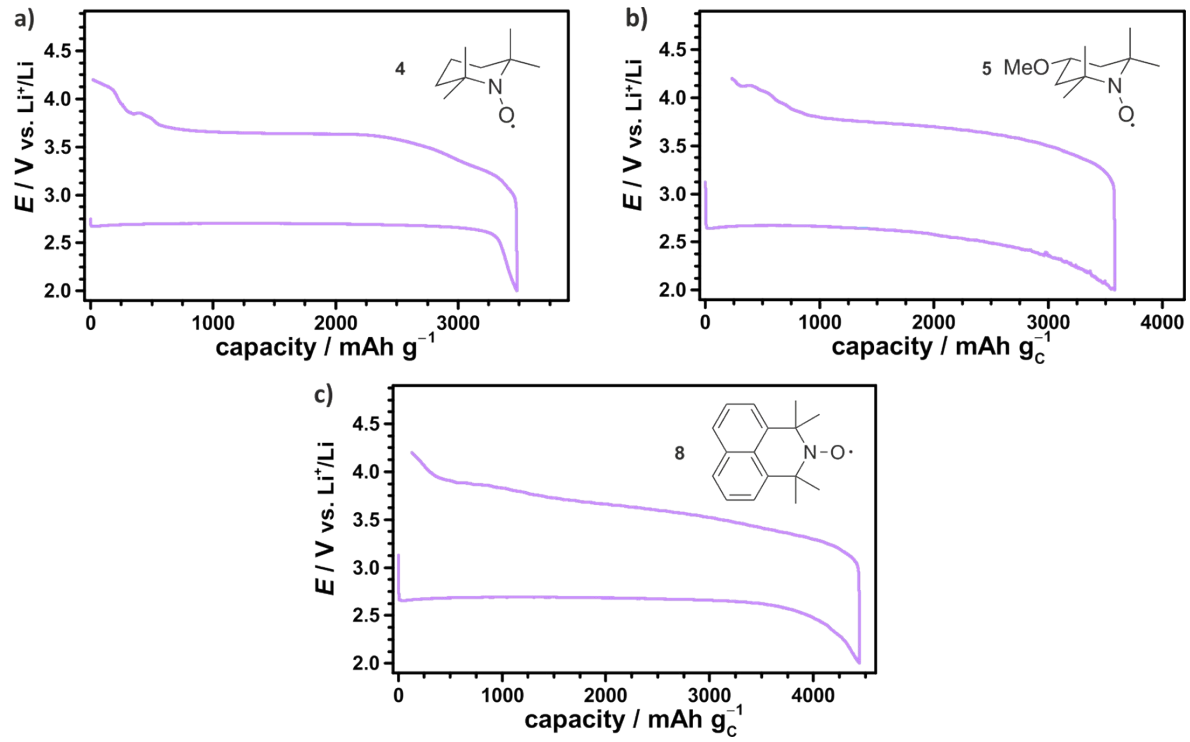

Fig. S6 Cycling profiles of Li-O_2 cells with 10 mM **a)** TEMPO **4**, **b)** 4-methoxy-TEMPO **5**, **c)** TMAO **8** in 1 M LiTFSI/diglyme; obtained with j = 0.1 mA cm^{-2}, $p(O_2)$ = 1bar and cut-off potentials of 2.0 V resp. 4.2 V vs. Li$^+$/Li. The corresponding profile of a Li-O_2 cell with pure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

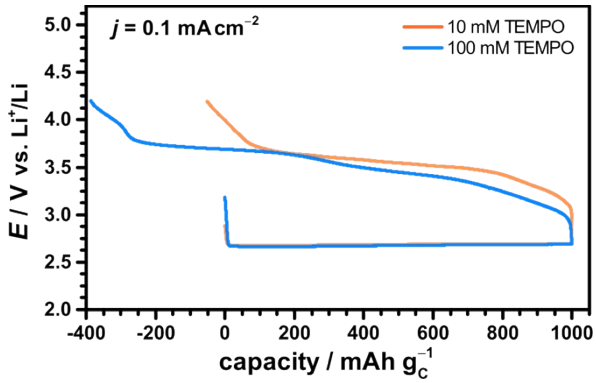

Fig. S7 Cycling profiles of Li-O_2 cells with 10 mM and 100 mM TEMPO in 1 M LiTFSI/diglyme using j = 0.1 mA cm^{-2}, $p(O_2)$ = 1bar and a fixed discharge capacity of $1000\ \mathrm{mAh\ g_C^{-1}}$.

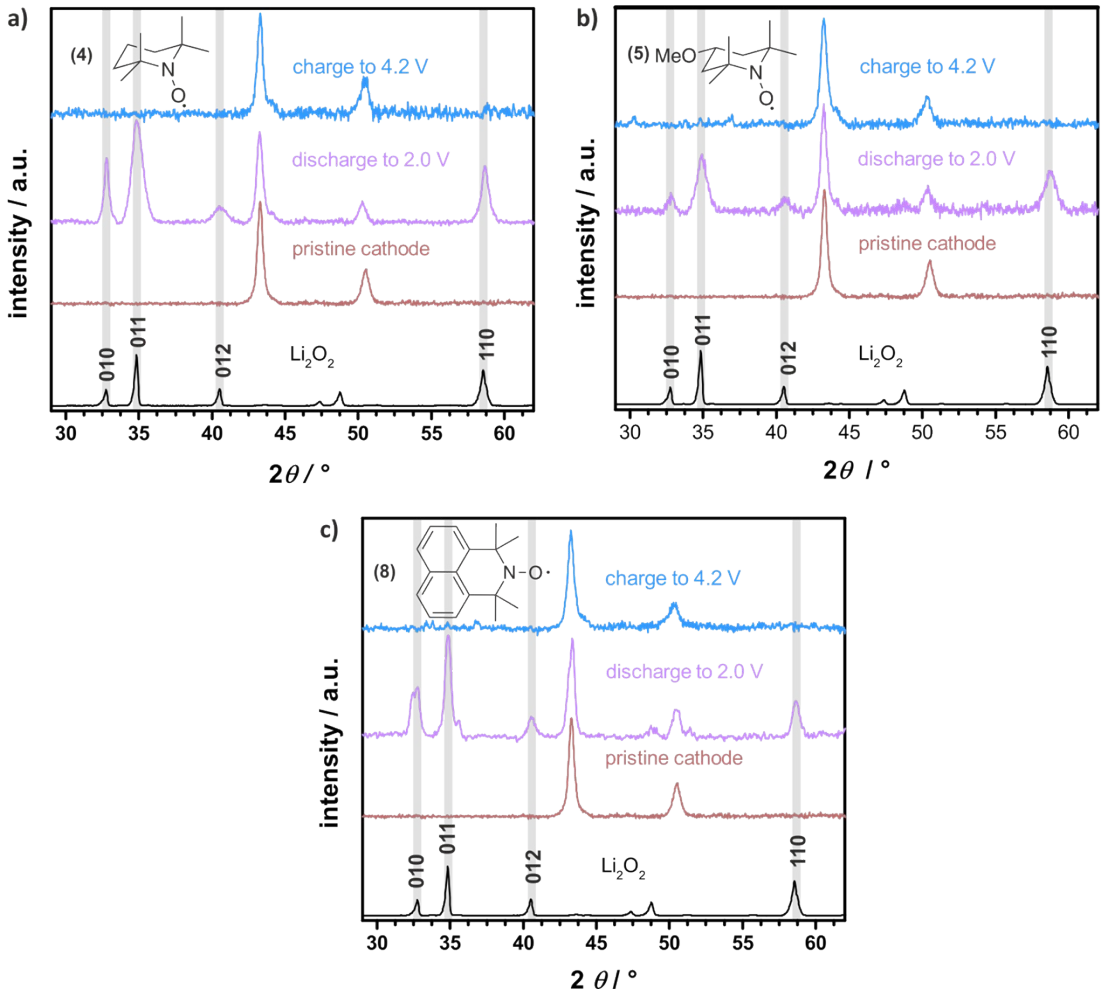

Fig. S8 XRD patterns of the carbon cathodes after discharge and charge in a Li-O_2 cell with 10 mM **a)** TEMPO **4**, **b)** 4-methoxy-TEMPO **5**, **c)** TMAO **8** in 1 M LiTFSI/diglyme; the corresponding cycling profiles are illustrated in Fig. S6. Li_2O_2 diffraction pattern matches the typical Li_2O_2 faces (ICSD 98-018-0557).