

ADVANCED MATERIALS

Supporting Information

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A High-Performance Li–O₂ Battery with a Strongly Solvating Hexamethylphosphoramide Electrolyte and a LiPON-Protected Lithium Anode

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Materials. Hexamethylphosphoramide (HMPA), tetra ethylene glycol dimethylether (TEGDME) and dimethyl sulfoxide (DMSO) were distilled under vacuum over CaH₂. Dimethoxyethane (DME) and acetonitrile (ACN) were distilled under argon over CaH₂. All solvents were further dried for several days over freshly activated molecular sieves (type 3Å) resulting in a final water content of ≤ 10 ppm (determined by Mettler-Toledo Karl Fischer titration apparatus). Battery grade lithium perchlorate (LiClO₄) was dried under vacuum at 140 °C for 24 h. All materials were stored in an argon-filled glove box (both H₂O and O₂ < 0.1 ppm).

Li-O₂ cell assembly and electrochemical measurements. Electrochemical measurements were conducted using a Biologic VMP3 electrochemical workstation. A multiple-necked, air-tight glass cell with valves to control the gas inlet and outlet was used throughout. Glassy carbon (GC, diameter 3 mm), partially delithiated LiFePO₄ composite electrode (Li_{0.5}FePO₄) and Pt wire were used as working, reference and counter electrodes, respectively. The working electrode was polished with 0.05 μm alumina slurry prior to use. The LiFePO₄ reference electrode was constructed by mixing LiFePO₄ with Super P (Timcal) and PTFE in a mass ratio of 8:1:1. The mixture was then pressed onto a stainless steel mesh and dried under vacuum at 120 °C for 24 h. The as-prepared reference electrodes were pre-oxidized (50 % of total capacity) to Li_{0.5}FePO₄, which has a stable potential of 3.45 V vs. Li/Li⁺. The electrochemical performance of Li-O₂ cells was examined using a Swagelok-type cell. A lithium metal foil (80 μm thick) protected by a LiPON film (specifically, 2.0 μm thick

$\text{Li}_{3.3}\text{P}_{1.0}\text{O}_{3.9}\text{N}_{0.17}$) was prepared by radio frequency sputtering, and the obtained LiPON film has a Li^+ ion conductivity of $\sim 2 \times 10^{-6} \text{ S cm}^{-1}$. Porous O_2 cathode was prepared by casting a slurry of Ketjen Black carbon (EC600-JD) and PTFE (9:1 wt/wt) dispersed in 2-propanol onto a stainless steel mesh and dried under vacuum at 110°C for 24 h. The mass loading of Ketjen Black was $1\text{-}5 \text{ mg cm}^{-2}$. The cells were assembled in an Ar-filled glove box. A glass fiber soaked with $60 \mu\text{L}$ electrolyte (0.1 M LiClO_4 in HMPA, TEGDME or DME) was placed between the anode and cathode. The cell was placed in a home-made glass tube equipped with gas inlet an outlet and sealed with high hermetic integrity. High purity O_2 was purged through the glass tube for 20 min to make a pure O_2 atmosphere. The galvanostatic discharge-charge tests were conducted on a LAND CT2001A battery testing system. The specific capacity was calculated based on the carbon mass of the cathode.

DEMS measurements of Li- O_2 cells. The DEMS system was built in-house. It was based on a commercial quadrupole mass spectrometer (Hiden Analytical) and a home-made Swagelok type DEMS cell with two PEEK capillary tubes as purge gas inlet and outlet. The flow rate of purge gas was controlled by a digital mass flow meter (Bronkhorst). The details of the purging system and the DEMS cell were shown in Figure S14 and Figure S15, respectively. During the discharging process, a mixture of Ar/ O_2 (molar ratio 1/4) with a flux of 1 mL min^{-1} was used as the working gas for the purpose of quantifying O_2 consumption. For charging process, 1 mL min^{-1} of high purity Ar was used as carrier gas. In either case, Ar acts as the internal tracer gas with known invariable flux. The DEMS cell was controlled by a LAND CT2001A battery testing system or a Princeton PARSTAT 4000 electrochemical workstation.

Instruments and characterization. Powder X-ray diffraction was performed on a Bruker D8 ADVANCE X-ray diffractometer with Cu $K\alpha$ ($\lambda=1.54 \text{ \AA}$) radiation. During measurements, the discharged cathodes were contained in a homemade airtight sample holder. Scanning electron microscopy was performed on a field emission FEI XL-30 instrument, operating at an accelerating voltage of 10 kV. FTIR measurements were carried out on a Nicolet iS5

spectrometer (Thermo Fisher Scientific) housed in an argon-filled glove box and operated in transmission mode. The electrolytes after various cycle numbers were collected by washing the glass fiber separators with CDCl_3 , and subjected to ^1H and ^{13}C NMR (Bruker, 500 M). ESI-MS (Thermo LTO Orbitrap) was employed to investigate the solvation of Li_2O_2 in HMPA. The solubility of Li_2O_2 in different solvents was determined by inductively coupled plasma mass spectrometry (ICP-MS) on a Thermo Scientific X Series II instrument. The saturated Li_2O_2 (Li_2CO_3 or LiOH) solutions were prepared by mixing 50 mg of Li_2O_2 with 5 mL of solvents in an Ar-filled glove box under vigorous stirring for 8 h. The obtained suspensions were centrifuged at 10000 rpm for 10 min, and the supernatants were collected for ICP-MS measurement.

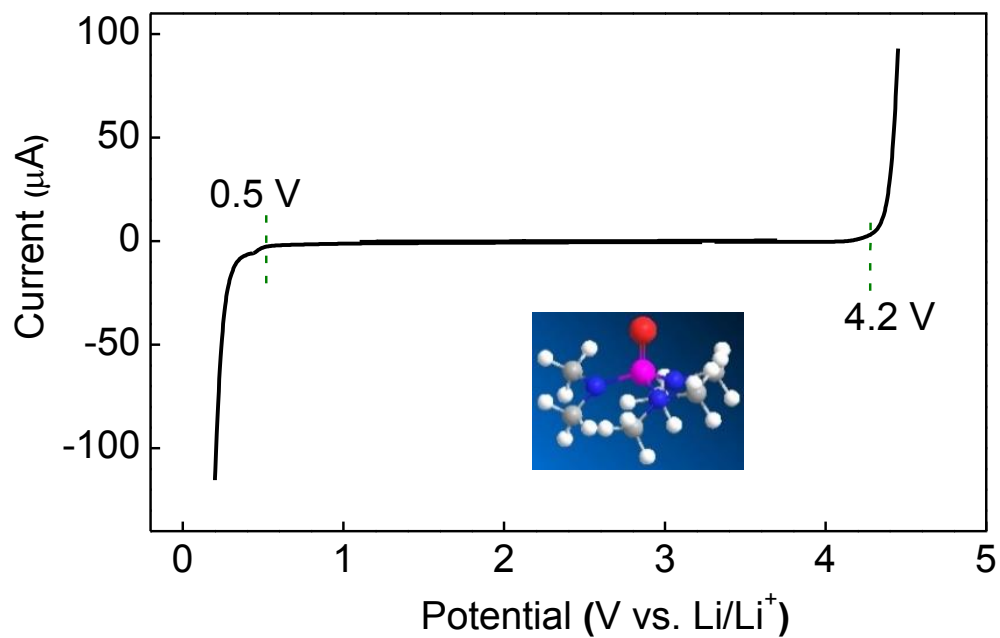


Figure S1. Linear potential scan conducted at a glassy carbon electrode in 0.1 M LiClO₄ HMPA, scan rate 25 mV s⁻¹. Inset shows the molecular structure of HMPA, red: O, purple: P, blue: N, grey: C, and white: H.

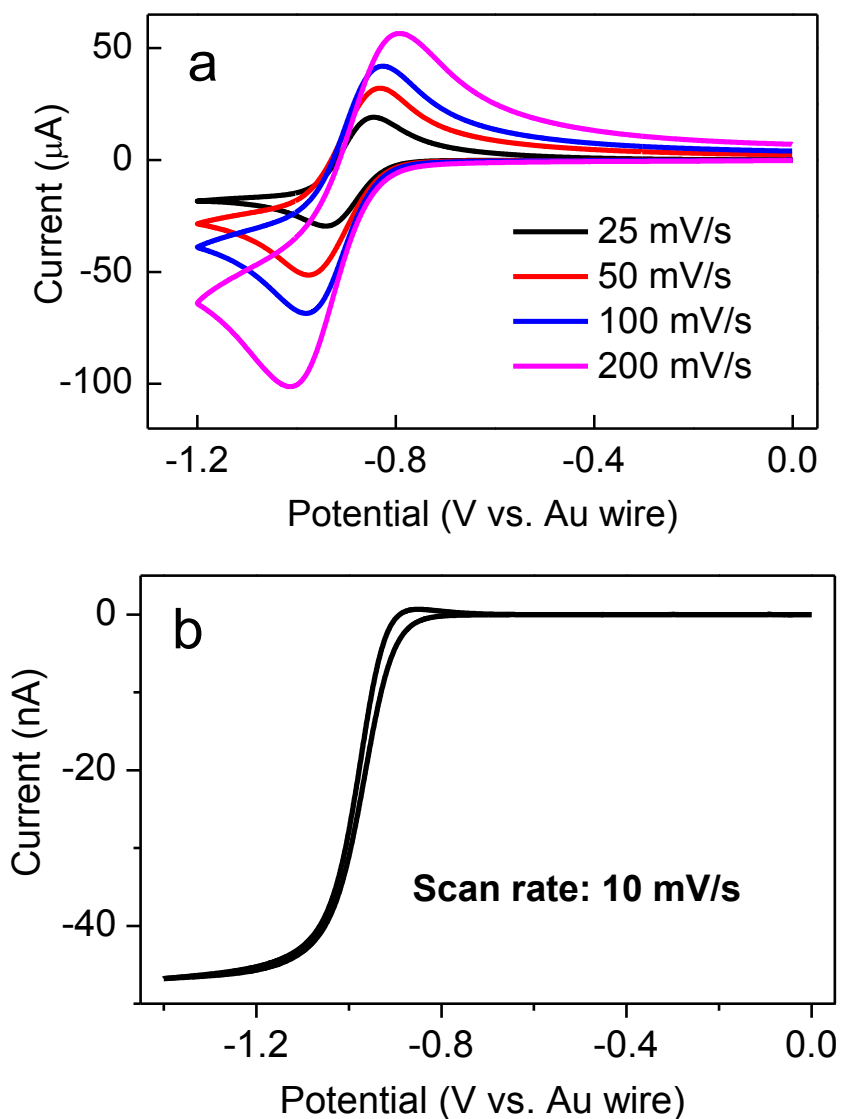


Figure S2. A combination of a) cyclic voltammetry at glassy carbon disk electrode (diameter 3 mm) and b) potential polarization at carbon fibre micro disk electrode (diameter 25 μm) in O_2 saturated 0.1 M TBAClO_4 HMPA was used to determine the solubility and diffusion coefficient of dissolved O_2 . See text book of *Electrochemical Methods: Fundamentals and Applications* by A.J. Bard and L. R. Faulkner for technique details.

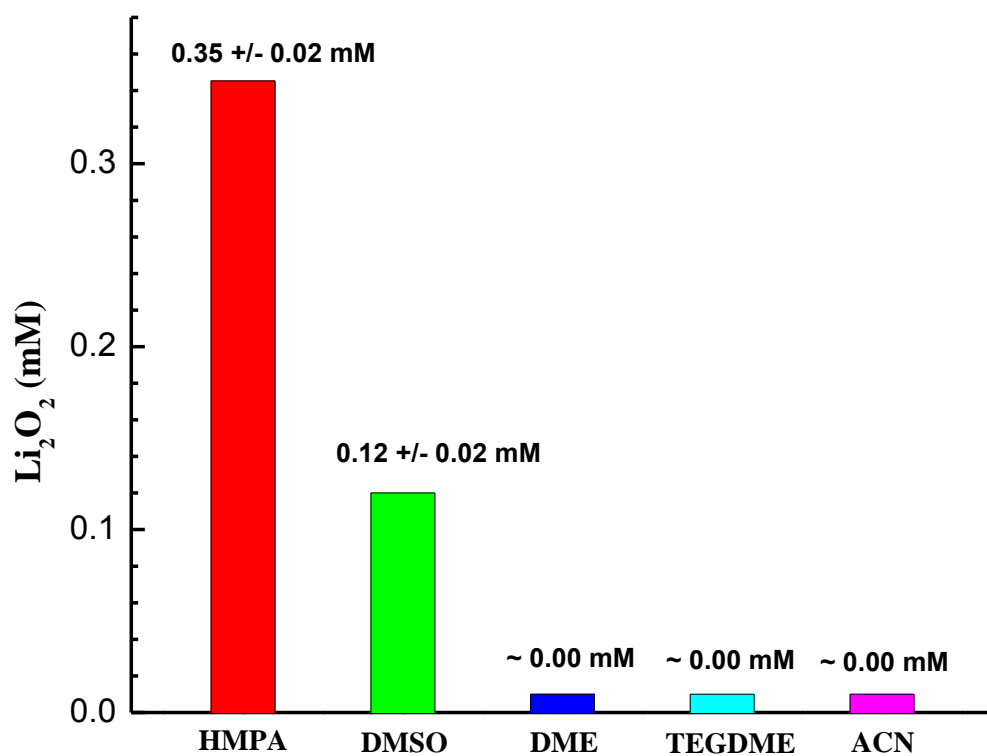


Figure S3. Saturated concentrations of dissolved Li_2O_2 in HMPA, DMSO, DME, TEGDME and ACN. Based on the system error of the ICP-MS protocol used in this study, the concentrations of dissolved Li_2O_2 in DME, TEGDME and ACN are too low to be determined with precision, and therefore can be thought to be ~ 0.00 mM.

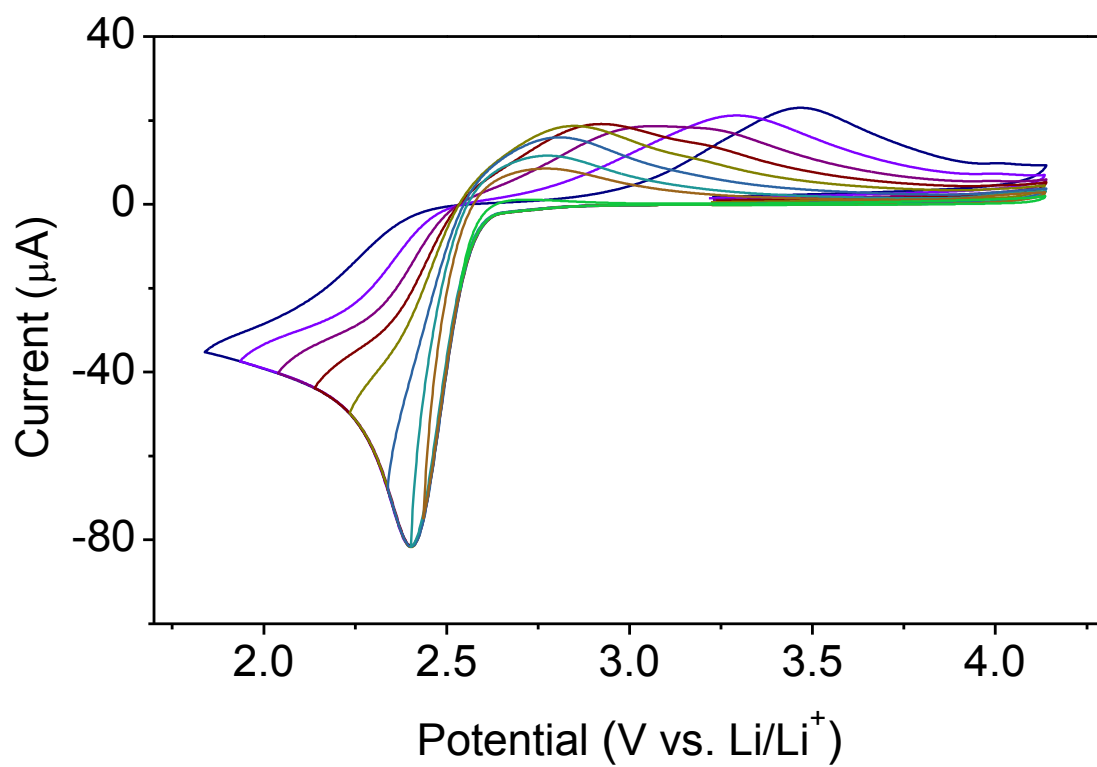


Figure S4. CVs on glassy carbon electrode (diameter 3 mm) in O₂ saturated 0.1 M LiClO₄ HMPA with different cathodic cutoff potentials at a scan rate of 0.1 V s⁻¹.

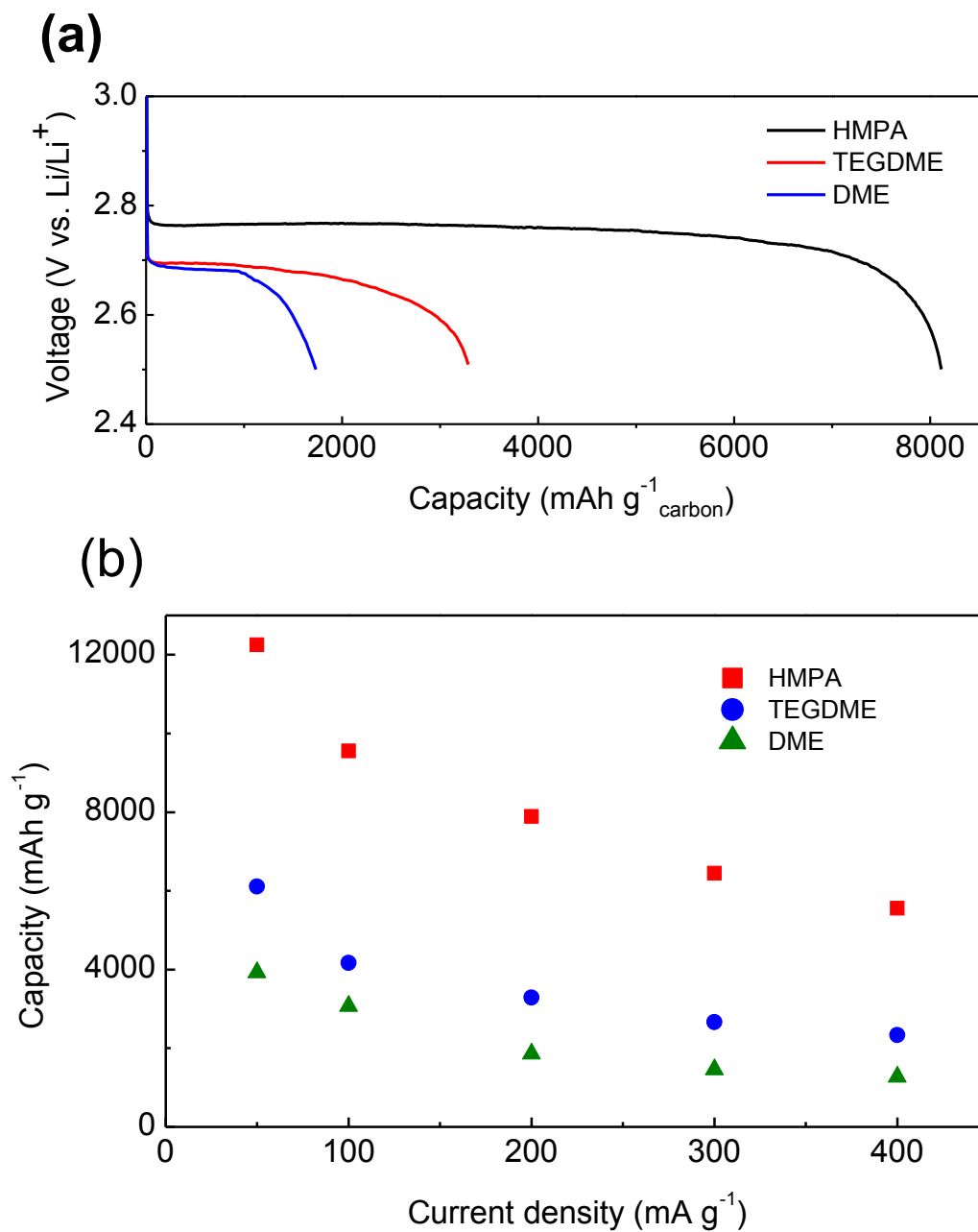


Figure S5. a) Discharging of Li-O₂ batteries with HMPA (black), TEGDME (red) and DME (blue)-based electrolytes with a cathodic cutoff potential of 2.5 V at a current density of 200 mA g⁻¹ carbon. b) Rate performance of the Li-O₂ cells with HMPA, TEGDME and DME electrolytes.

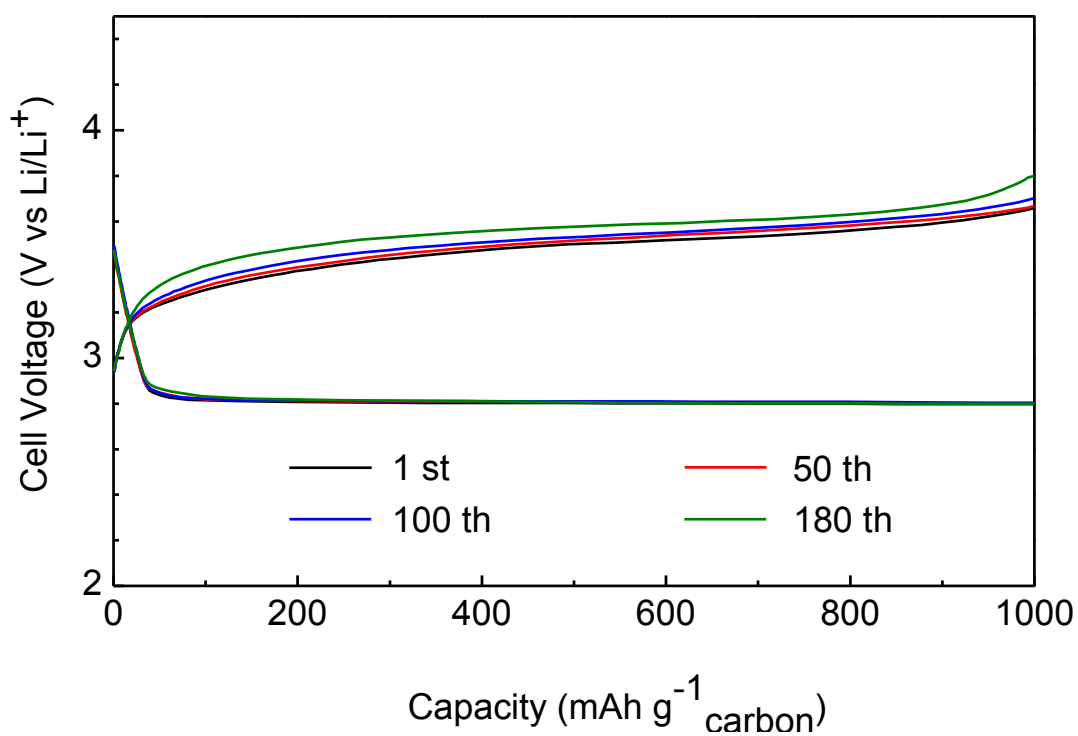


Figure S6. Charge/discharge curves of a Li-O₂ cell with a 0.1 M LiClO₄ HMPA electrolyte at a current density of 200 mA g⁻¹ carbon.

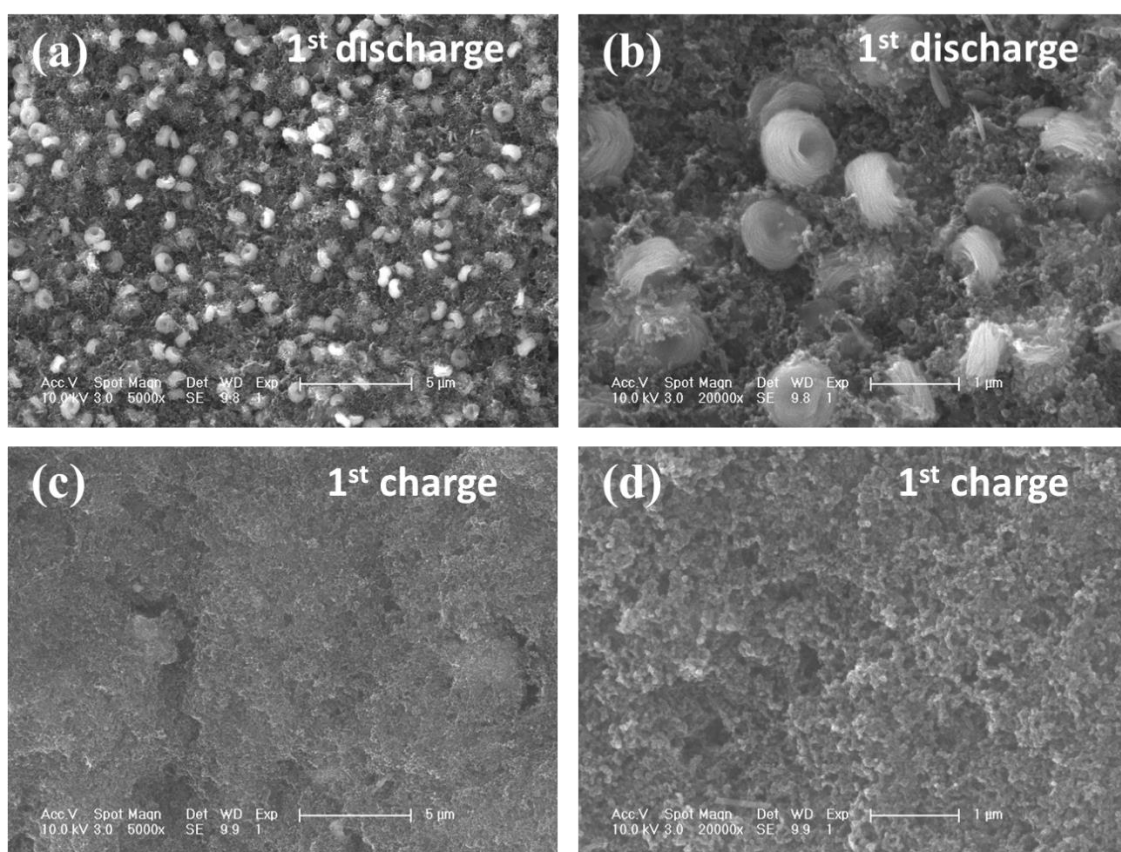


Figure S7. SEM images of the 1st discharged (a, b) and charged (c, d) cathodes of the HMPA-based Li-O₂ cells.

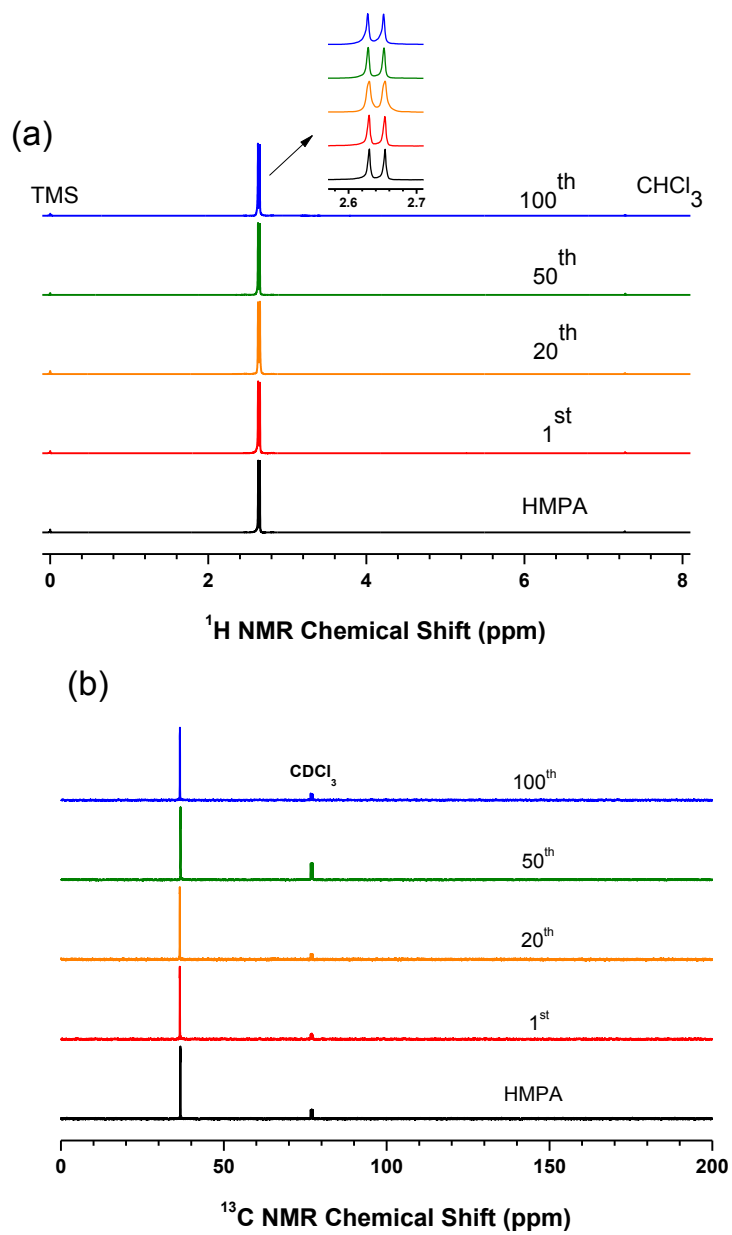


Figure S8. a) ¹H and b) ¹³C NMR study of the electrolyte in the HMPA-based Li-O₂ cells after cycles of 1, 20, 50 and 100.

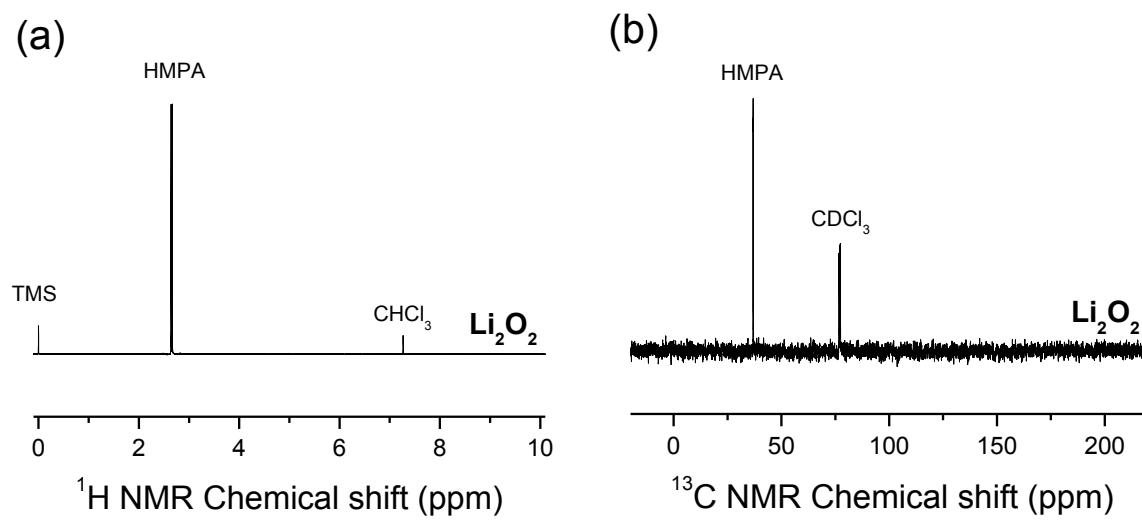


Figure S9. a) ^1H and b) ^{13}C NMR study of the HMPA solvent after reacting with Li_2O_2 for 1 week.

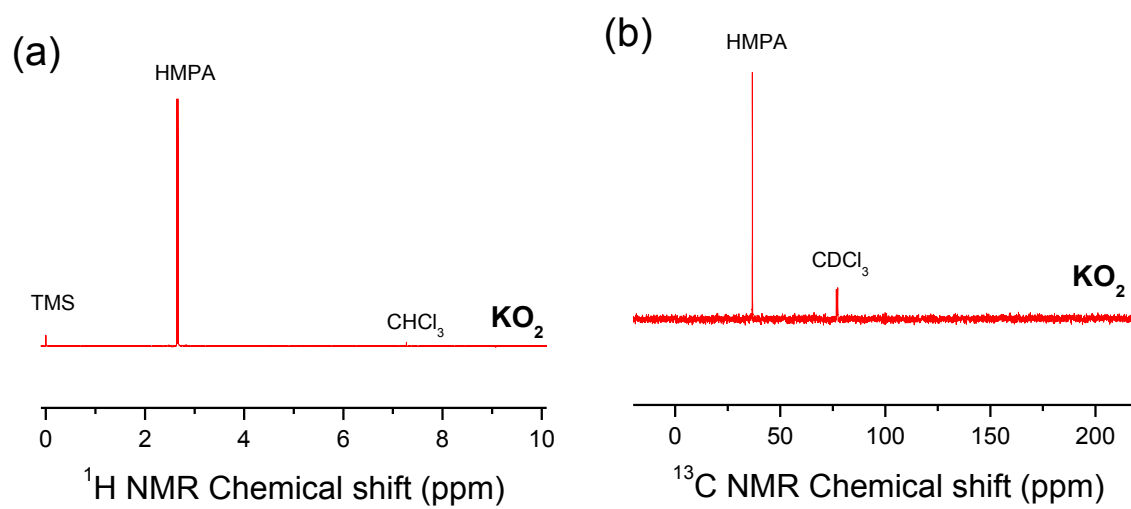


Figure S10. a) ^1H and b) ^{13}C NMR study of the HMPA solvent after reacting with KO_2 for 1 week.

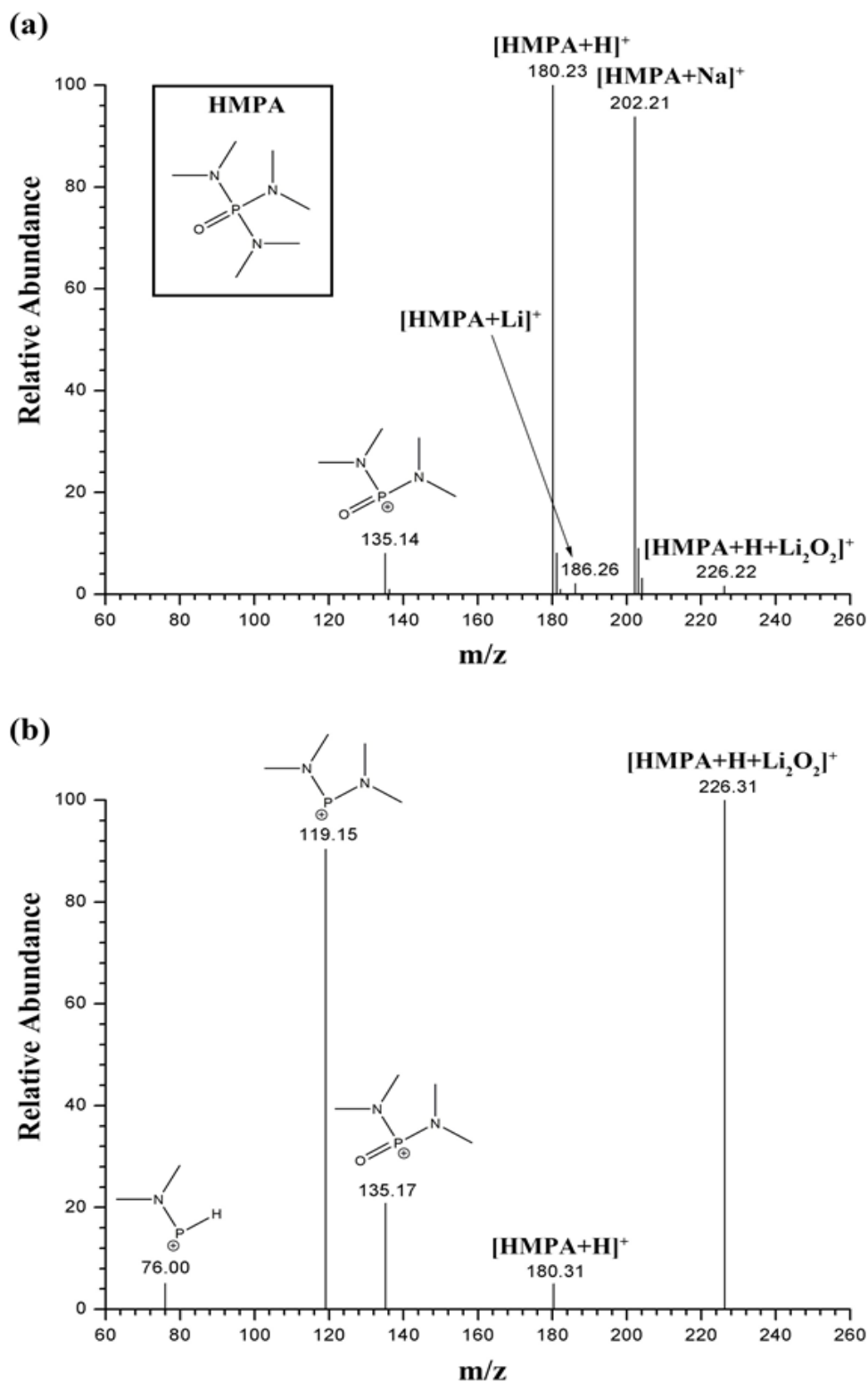


Figure S11. a) An overall ESI-MS scan of Li_2O_2 -saturated HMPA identifying 1:1 complexes of Li_2O_2 and HMPA ($m/z = 226$). b) Tandem MS study of the Li_2O_2 -HMPA complexes. ACN solvent was used to dilute the Li_2O_2 -saturated HMPA. Na^+ ions were from the system background, which have been widely observed in many other ESI-MS experiments (Anal. Chem. 2007, 79, 4013-4021 and references therein).

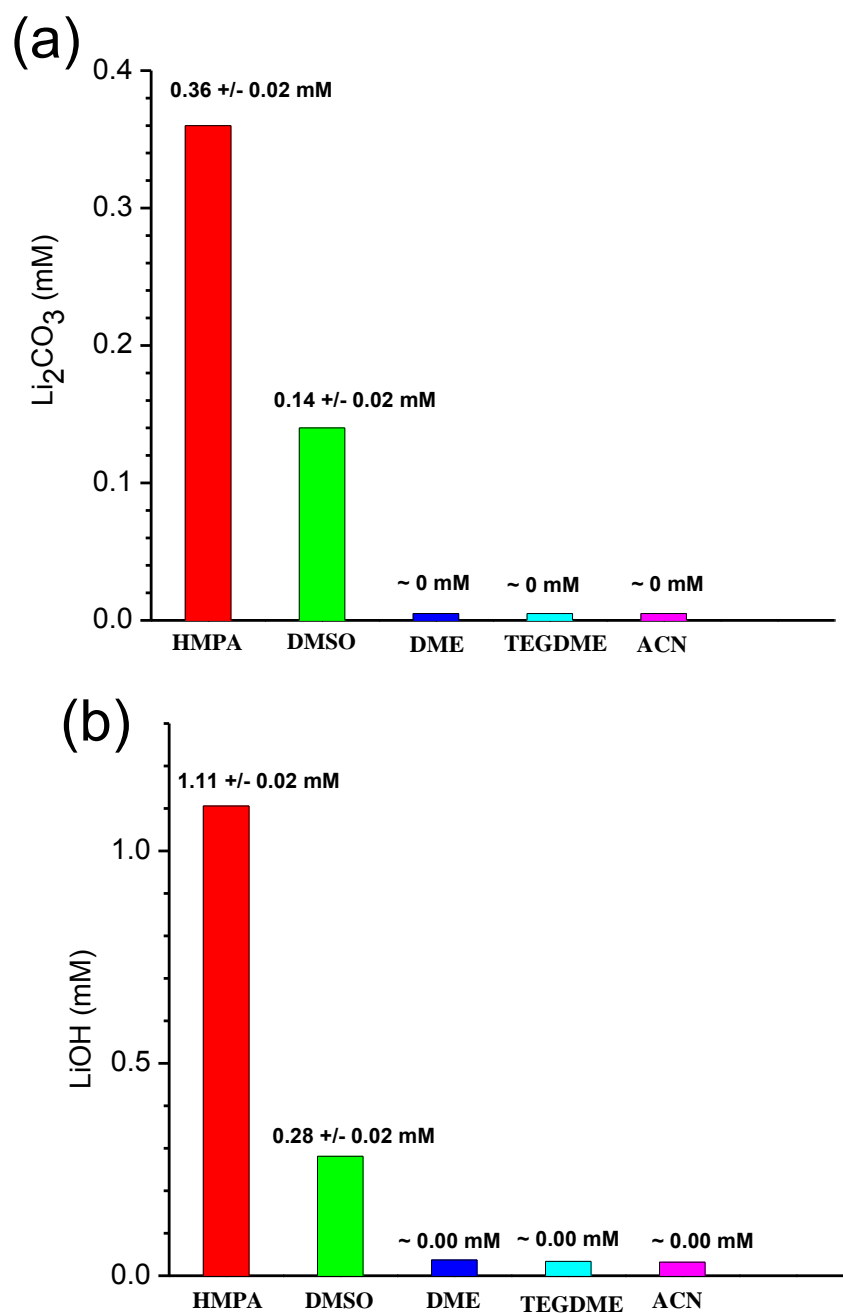


Figure S12. Saturated concentrations of dissolved a) Li₂CO₃ and b) LiOH in HMPA, DMSO, DME, TEGDME and ACN. Based on the system error of the ICP-MS protocol used in this study, the concentrations of Li₂CO₃ and LiOH in DME, TEGDME and ACN are too low to be determined with precision, and therefore can be thought to be ~ 0.00 mM.

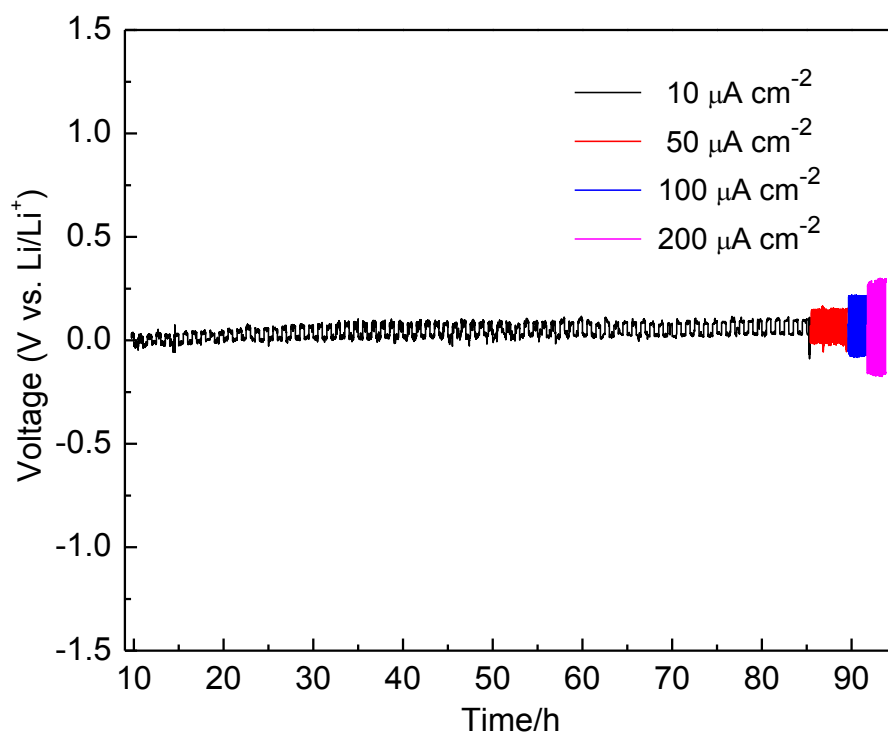


Figure S13. Cycling of a symmetrical cell of Li|LiPON-LiPON|Li containing 0.1 M LiTFSI HMPA at various current densities.

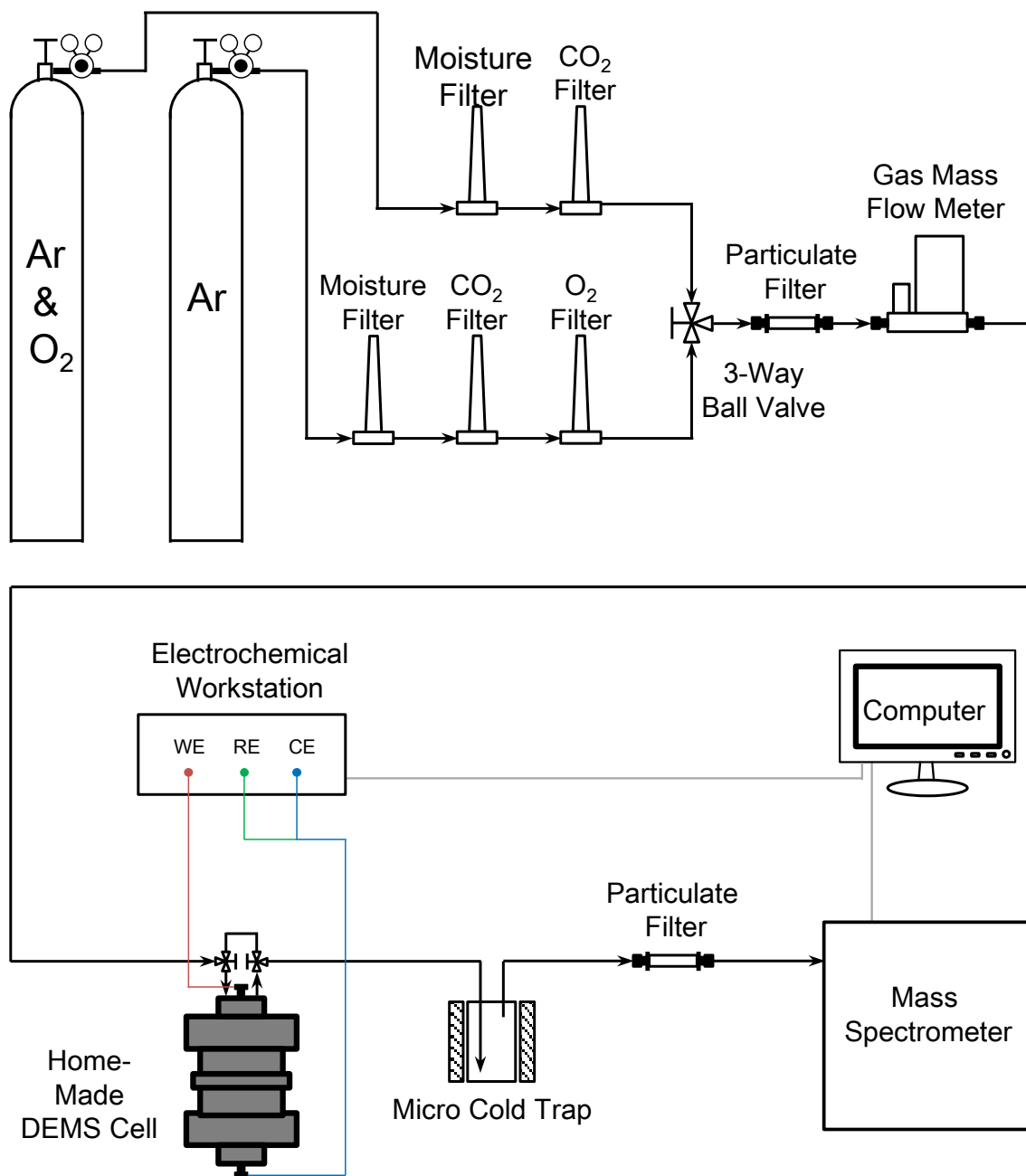


Figure S14. Schematics of the DEMS system.

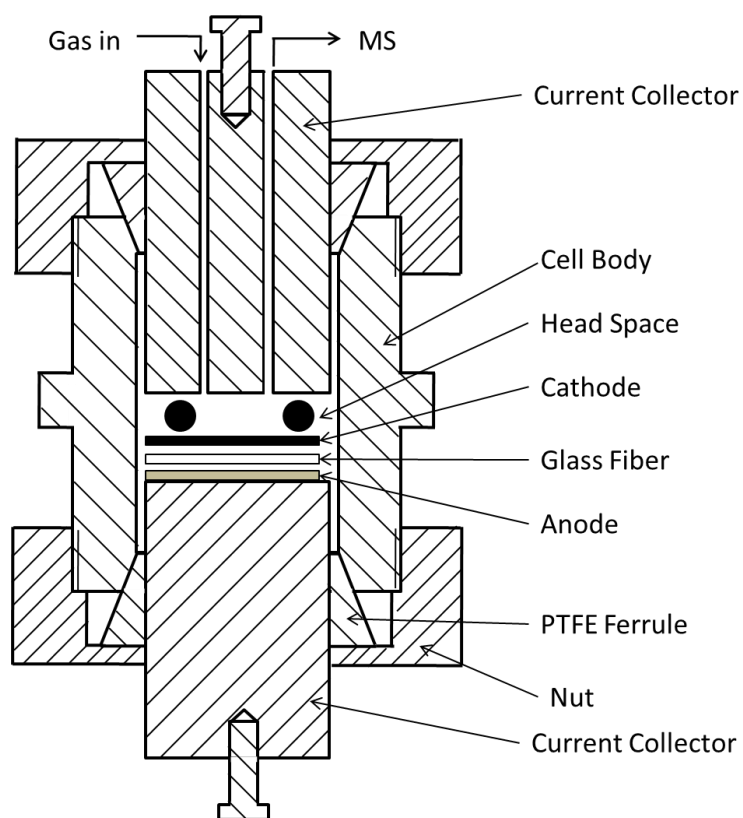


Figure S15. Schematics of the home-made Swagelok type DEMS cell.

Table S1. O₂ electrochemistry quantified by DEMS: ratios of the number of electrons to oxygen molecules upon reduction (discharge) and oxidation (charge) and oxygen recovery efficiency.

Cycle number	Discharge e ⁻ /O ₂	Charge e ⁻ /O ₂	O ₂ recovery efficiency
1	1.99	2.03	0.95
20	2.04	2.01	0.98
50	2.03	2.06	1.02
100	2.05	2.02	0.96

Table S2. Donor numbers of several solvents.

Solvent	Donor Number
HMPA	38.8 ^a
DMSO	29.8 ^a
DME	20.0 ^b
TEGDME	16.6 ^b

^aW. B. Jensen, *Chem. Rev.* **1978**, 78, 1.

^bC. O. Laoire, S. Mukerjee, K. M. Abraham, E. J. Plichta, M. A. Hendrickson, *J. Phys. Chem. C* **2010**, 114, 9178.