Avoiding the Irreversible Four-electron Reduction of Oxygen in Water-containing Lithium-air Batteries

Conrad Holc[1,2,3], Rory C. McNulty[1,3], Jack W. Jordan[1,3], Ganesh Vailaya[1], Daniel Dewar,[2,3]

Graham N. Newton[1,3], Darren A. Walsh[1,3], Peter G. Bruce[2,3*], Lee R. Johnson[1,3*]

[1] Nottingham Applied Materials and Interfaces Group, School of Chemistry, University of Nottingham, NG7 2TU, UK

[2] Departments of Materials and Chemistry, Parks Road, University of Oxford, OX1 3PH, UK

[3] The Faraday Institution, Quad One, Harwell Science and Innovation Campus, Didcot, OX11 0RA, UK

* Lee.johnson@nottingham.ac.uk, peter.bruce@materials.ox.ac.uk

Supplementary information

Materials and methods

Dimethyl sulfoxide (DMSO >99.5%, Aldrich) was used as supplied. Tetraethylene glycol dimethyl ether (TEGDME >99.5%, Aldrich) was distilled over benzophenone and sodium under vacuum. (DME >99.5%, Aldrich) was distilled over benzophenone and sodium under argon. For 500 ml of ether solvent, 9 g of benzophenone and 1.5 g of sodium was used. Distilled solvents were further dried for several days over freshly activated molecular sieves (type 4Å, Aldrich) before use. The final water content was ≤4 ppm (determined by Karl Fischer titration). Lithium perchlorate ($LiClO_4$, 99.99%, Aldrich), tetrabutylammonium perchlorate ($TBAClO_4$, ≥99%, Aldrich) potassium dioxide (KO_2, 97%, Aldrich), 2,5-di-tert-butl-1,4-benzoquinone (DBBQ, 99%, Aldrich), ferrocene methanol (FcMeOH, 97%, Aldrich), and 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO, 98%, Aldrich) were used as supplied without further purification. An O_2 gas line comprising of high purity O_2 (BOC, Grade N5.5) and a moisture trap (Agilent) was used in all measurements. Triethylphosphine oxide (Et_3PO, Acros Organics) was dried by dissolution in dichloromethane and addition of activated molecular sieves. Once dry, Et_3PO was recovered by evaporation of dichloromethane in a glovebox. Diphenylphosphinic chloride (Ph_2POCl, Sigma) was used as received. H_2O_2 (30% wt. in H_2O, Fisher) was used fresh and as provided. All cell components were dried at elevated temperature under vacuum and transferred to a N_2-filled glovebox (MBraun, O_2 ≤0.1 ppm, H_2O ≤0.1 ppm) without exposure to air. All electrolytes were prepared within a N_2-filled glove box and to a salt concentration of 0.25 M. Dry electrolytes contained <10 ppm H_2O (determined by Karl Fischer titration). H_2O-solvent mixture electrolytes were prepared using deionised water (18.2 MΩ cm, MilliQ).

3-electode electrochemical measurements were performed using an SP300 potentiostat (Biologic) and a multi-necked, airtight glass cell within an N_2-filled glove box. Electrochemical measurements were carried out at room temperature and *iR* correction was used. A platinum wire served as the counter electrode (CE). Measurements were performed using a reference electrode based on $LiFePO_4$

(LFP), which was pre-oxidized (20% of total capacity) to Li_xFePO_4. This was placed in 0.1 M $LiClO_4$, 1 M $TBAClO_4$ in DMSO separated from the bulk electrolyte with a porous frit, thus providing a fixed potential. Glassy carbon (GC) was used as the working electrode for voltammetry on carbon. Steel mesh (316 grade, Advent) was cut into flag electrodes (0.5 cm^2) for voltammetry on stainless steel (SS) electrodes. Electrolytes were saturated with O_2 by bubbling the gas through the liquid for approximately 3 minutes. Where an internal reference was required, ferrocene methanol was added to the electrolyte.

RDE measurements were recorded using a 3-electrode configuration consisting of either a 5 mm glassy carbon (GC) or SS working disk electrode (ChangeDisk, Pine Instruments), a fritted LFP reference electrode, and a Pt counter electrode. The disk electrodes were polished separately to prevent cross-contamination. The GC and SS disk electrodes were mechanically polished by hand using 0.1 µm alumina powder (Buehler) on a neoprene polishing pad. The electrode was then briefly sonicated in H_2O to remove any residual alumina on the surface, before being dried under vacuum at 70 °C and transferred to a N_2-filled glovebox for cooling. Once the electrodes were cool, the RDE was assembled. 10 mL of electrolyte was used for each measurement. H_2O_2 measurements were carried out under an N_2-atmosphere, with no O_2 sparging of the electrolytes. A 5 mM H_2O_2 concentration was obtained by the addition of 30 wt.% H_2O_2 solution and H_2O in the required ratio to achieve the desired H_2O concentration.

On-line mass spectrometry measurements were recorded on an instrument built in-house by the University of Nottingham Mechanical Workshop coupled to a quadrupole mass spectrometer (Hiden Analytical). For chemical disproportionation experiments, a MS vial was filled with a known quantity of KO_2 (ca. 5 mg) in an Ar-filled glovebox and capped with a rubber bung. The vial was then transferred onto an isolated section of the flow line before the line was opened, allowing Ar (99.999%, CK Isotopes) to flow through the headspace of the vial. The MS signals were allowed to reach equilibrium before the disproportionation reaction was initiated by the addition of the desired electrolyte mixture. Cell measurements were recorded with a cell manufactured by the University of Nottingham Mechanical workshop on the same instrument. The cell housed a 24 mm freestanding LFP anode and a porous carbonaceous cathode, electrically isolated by two 26 mm glass fibre separators. SS mesh was placed on top of the cathode to ensure good electrical contact. The electrolyte volume used in these measurements was 800 µL. Prior to discharge, the cell was assembled in a N_2-filled glovebox. The headspace was then purged with a 20% O_2/80% Ar gas mixture (99.999%, CK Isotopes) for at least 24 hours, or until the mass signals had reached equilibrium, ensuring that the electrolyte had reached equilibrium concentration with the headspace. Where humid gas streams were required, humidifying solutions were attached upstream of the DEMS cell to bubble the carrier gas through. Where 100% relative humidity was required, gas was diverted through a solution of H_2O, and where a 13% relative humidity was desired, gas was diverted through a solution of saturated LiCl in H_2O.[1]

Pressure cell measurements were performed using a Swagelok-type cell of 24 mm diameter and incorporating a pressure sensor (Omega Engineering). Two 24 mm gas diffusion layers (GDLs, H23, Quintech) served as the air-electrode. Two 26 mm glass fibre filters (Whatman) were used as the separator. Freestanding 24 mm Li_xFePO_4 counter electrodes (pre-oxidized to 20% of total capacity) were prepared using 80 % w.t. $LiFePO_4$, 10 % w.t. carbon (Super P, Timcal Ltd) and 10 % w.t. PTFE (Sigma-Aldrich). SS mesh acted as a current collector for the air-electrode. Cells were discharged with 800 µL of electrolyte. Prior to discharge, the cell headspace was purged with O_2 (N5.5, BOC) for a total time of 3 minutes. A constant purge was employed for cells containing DMSO- and TEGDME-based electrolytes. An alternating flow on bypass and through cell was employed for cells containing a DME-based electrolyte to mitigate DME evaporation. Cells containing DME were discharged once the cell pressure had reached equilibrium. Cycling was performed on an Octostat30 potentiostat in an

incubator at 20 °C. The cell volume was determined post-discharge using a calibration tube of known volume.

Li_2O_2 yield measurements were performed on electrodes discharged to a capacity of 0.44 mAh cm^{-2} on 12 mm GDL air electrodes using the same cell configuration as described above (12 mm LFP, 14 mm separator, 12 mm SS mesh) in 12 mm Swagelok cells in rifle configuration, with 200 µL of electrolyte. Cycling was performed on an Octostat30 potentiostat in an incubator at 20 °C. Li_2O_2 amounts were determined by UV-Vis spectrometry using a titration method reported previously.[2–4] The cathode and separator were extracted from a discharged cell and added to a vial containing a known quantity of MilliQ H_2O. A known volume of this solution was then mixed in a 1:1 ratio with a solution of 2 wt.% titanium(IV) oxysulfate ($TiOSO_4$, Aldrich) in 1 M H_2SO_4 to achieve an optimum concentration of the coloured complex $[Ti(O_2)]^{2+}$ (λmax = 405 nm), which is formed in the presence of H_2O_2. The UV-Vis absorption spectrum was measured and compared to a calibration curve made from known concentrations of H_2O_2.

The concentration of H_2O in aprotic solvents in humid atmospheres was determined by placing a 0.25 M $LiClO_4$ TEGDME electrolyte into a sealed container filled with dry N_2 and an open beaker of H_2O, housed in an incubator at 20 °C. The solution was stirred with a magnetic stirrer bar and left to reach equilibrium. An internal humidity sensor (Omega Engineering) was used to record the relative humidity of the atmosphere. Aliquots of the electrolyte solution were analysed by Karl Fischer titration to determine the equilibrium water concentration at 20 °C and 100% relative humidity.

Acceptor numbers (ANs) of H_2O-solvent solutions were determined using the method described by Mayer *et al*.[5,6] Briefly, the ^{31}P chemical shift of Et_3PO is proportional to the solvent acceptor number and a calibration curve was constructed by recording ^{31}P NMR spectra of solvents with known AN containing Et_3PO, to convert chemical shift to the AN scale. All solvents were dried with molecular sieves prior to use. NMR samples were prepared in a N_2-filled glovebox and measurements were carried out in airtight NMR tubes (Young tap fitted) to prevent variation of the H_2O concentration. ^{31}P NMR spectra were recorded in solutions of varying H_2O content containing Et_3PO and the ANs were determined by comparing the ^{31}P chemical shift of Et_3PO to the calibration curve. NMR spectra were recorded on a Bruker Ascend 400 MHz NMR. Airtight NMR tubes were used to prevent variation of the H_2O concentration.

Chemical characterisation of discharged cathodes was performed by first discharging to a capacity of 2 mAh cm^{-2} in a 12 mm Swagelok rifle-cell. After discharge, cells were disassembled inside a N_2-filled glovebox, taking care to extract the top carbonaceous cathode. The electrode was thoroughly rinsed with dry DME, before being transferred to the glovebox antechamber under N_2 and dried under vacuum. The dried electrodes were then stored in sealed containment inside a N_2-filled glovebox prior to characterisation. Powder X-ray diffraction (PXRD) measurements were performed using a Malvern PANalytical X'Pert MPD operating in capillary spinner transmission mode equipped with a PIXcel area detector and a sealed tube Cu source operating at a tube voltage and current of 40 kV and 40 mA, respectively. A PW3152/63 focussing mirror was attached to eliminate Kβ wavelength radiation, resulting in a beam height of 0.7 mm at the sample position. The incident beam and diffracted beam pass through a pair of 0.04 rad Soller slits to reduce axial beam divergence. A fixed mask matching the prepared sample width and a fixed 1° anti-scatter slit were used in the incident beam path. Scans were performed from 30-70° in capillary spinning mode. Each spectrum was recorded over 30 minutes. A total measurement time of 1 hour (2 × 30-minute) was used to characterise the discharge product of cells that contained no redox mediators. A total measurement time of 12 hours (24 × 30-minute) was used to characterise the discharge product of cells that contained DBBQ and TEMPO. Samples were prepared for XRD analysis by slicing the electrode into thin strips and inserting them into a glass capillary (SGCT 1.5 mm, Capillary Tube Suppliers Ltd.) ensuring that the sample was located in the path

of the X-ray beam when mounted on the capillary spinner. The capillaries were sealed using Torr seal (Agilent) which was allowed to set for ≥12 hours before the capillary was removed from a N_2-atmosphere. Samples were aligned with the X-ray beam prior to analysis using a microscope attachment. The capillaries were spun throughout the entire measurement to enhance signal resolution. Fourier transform infra-red (FTIR) spectra were recorded on a Bruker Alpha II spectrometer with a Pt ATR module in a N_2-filled glovebox, without further manipulation of the dried electrode.

Steel-free perfluoroalkoxy alkane (PFA) Li-air cells consisted of a ½" diameter PFA Swagelok union with one ½" peek rod used to seal the bottom half of the cell, and a hollowed out peak cylinder used to hold the stacked cell in place. A schematic representation is shown in Figure S4. A carbon paper electrode with a long tail was placed below the 12 mm free standing LFP negative electrode to enable electrical connection. Two glass fibre separators were soaked in electrolyte (200 µL) and placed on top of the negative electrode. One 12 mm carbon paper electrode with a long tail was then placed on top of the separator stack, before a second 12 mm carbon electrode was placed on top and sealed in place with a hollow peak rod, wrapped in 125 µm PTFE. Electrical connection to the negative and positive electrodes was achieved by attaching clips to the tails of the relevant carbon paper electrodes. The PFA cell was stored in sealed containment with in a N_2-filled glovebox which was sparged with O_2 (N5.5, BOC). A glass bottle containing H_2O was also stored in this containment to ensure 100% relative humidity was maintained throughout the experiment. Cycling was performed on an Octostat30 potentiostat in an incubator at 20 °C.

Supplementary Figures

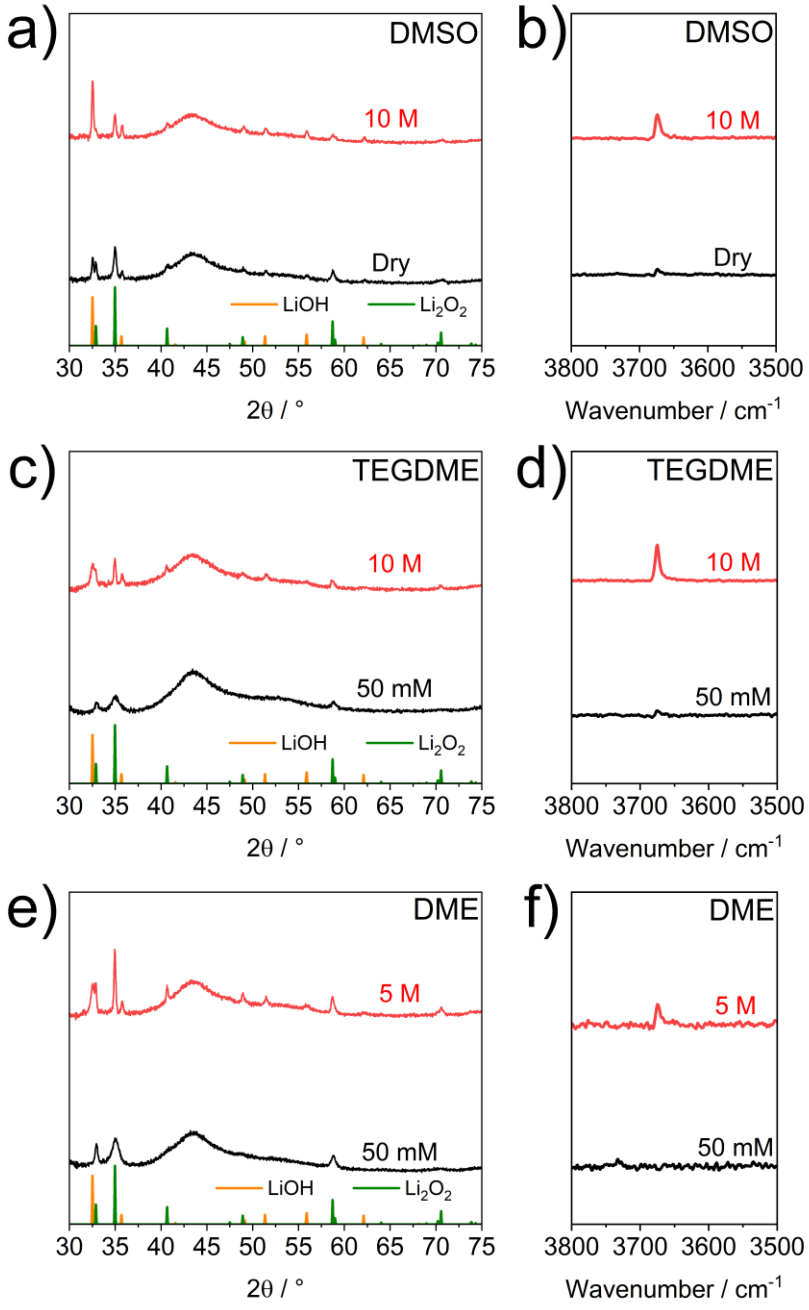

Figure S1| Chemical characterisation of discharge product from H_2O containing Li-O_2 cells. (**a, c, e**) PXRD and (**b, d, f**) FTIR characterisation of discharge products on the carbon positive electrode for cells containing DMSO, TEGDME, and DME. The H_2O concentration is indicated in the figure.

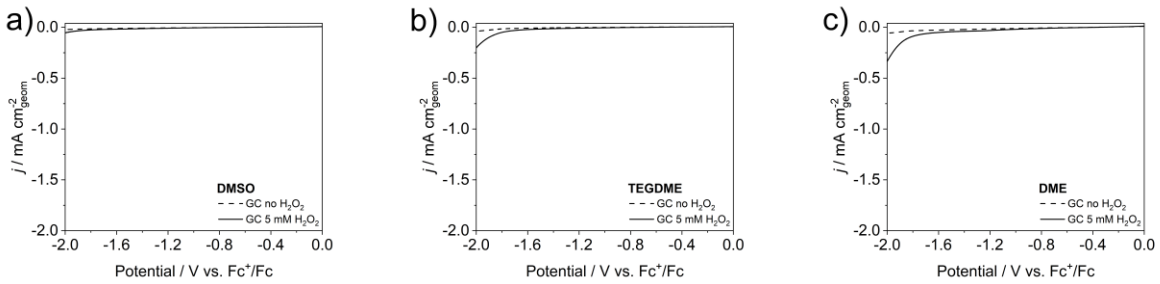

Figure S2| H_2O_2 electroreduction at carbon in H_2O-solvent electrolyte solutions. LSV measurements at carbon in 0.25 M $LiClO_4$ electrolytes containing 5 mM H_2O_2 in (**a**) DMSO (**b**) TEGDME (**c**) and DME. Measurements were performed using a glassy carbon (GC) working electrode, a Pt counter electrode and a fritted Li_xFePO_4 reference electrode at a rotation rate of 1000 rpm.

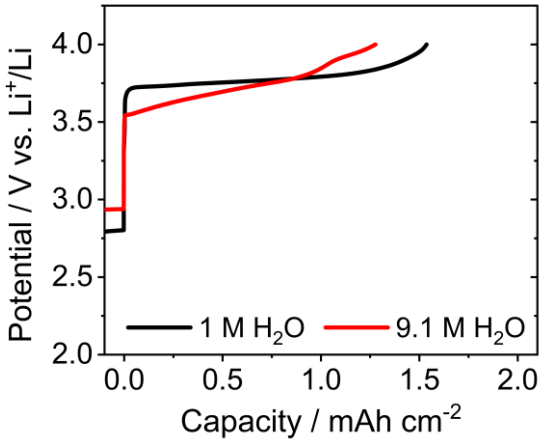

Figure S3| Voltage profiles of steel and H_2O containing Li-O_2 cells during charging.

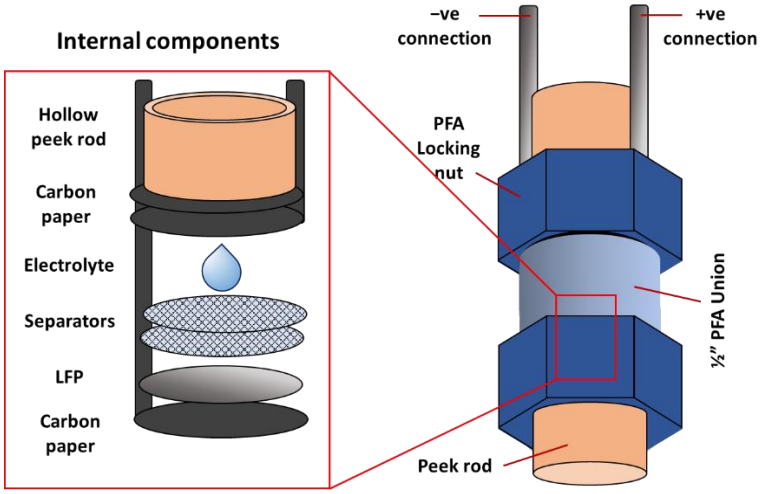

Figure S4| Schematic of steel-free cells. (**a**) The outer housing of the cell and (**b**) a cutout showing the current collectors, electrodes and separator.

References

1. Greenspan, L. Humidity Fixed Points of Binary Saturated Aqueous Solutions. *J. Res. Natl. Bur. Stand. Sect. Phys. Chem.* **81A**, 89–96 (1977).
2. Gao, X., Chen, Y., Johnson, L. & Bruce, P. G. Promoting solution phase discharge in Li–O2 batteries containing weakly solvating electrolyte solutions. *Nat. Mater.* **15**, 882–888 (2016).
3. Adelhelm, P. *et al.* A comprehensive study on the cell chemistry of the sodium superoxide (NaO2) battery. *Phys. Chem. Chem. Phys.* **15**, 11661 (2013).
4. O'Sullivan, D. W. & Tyree, M. The kinetics of complex formation between Ti(IV) and hydrogen peroxide. *Int. J. Chem. Kinet.* **39**, 457–461 (2007).
5. Mayer, U., Gutmann, V. & Gerger, W. The acceptor number — A quantitative empirical parameter for the electrophilic properties of solvents. *Monatshefte Für Chem. Chem. Mon.* **106**, 1235–1257 (1975).
6. Schmeisser, M., Illner, P., Puchta, R., Zahl, A. & Van Eldik, R. Gutmann donor and acceptor numbers for ionic liquids. *Chem. - Eur. J.* **18**, 10969–10982 (2012).