Supplementary Materials for

A Reversible and Higher-Rate Li-O_2 Battery

Zhangquan Peng, Stefan A. Freunberger, Yuhui Chen, Peter G. Bruce*

*To whom correspondence should be addressed. E-mail: p.g.bruce@st-andrews.ac.uk

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This PDF file includes:

Materials and Methods

Materials.

Dimethyl sulfoxide (DMSO) was distilled with addition of NH_2Na then further dried for several days over freshly activated molecular sieves (type 4Å) resulting in a final water content of ≤ 4 ppm (determined using a Mettler-Toledo Karl Fischer titration apparatus). Battery grade lithium perchlorate ($LiClO_4$) and lithium bis(trifluoromethane)sulfonimide salt (LiTFSI) were used for preparing the electrolytes as they can be obtained in high purity. Prior to use, both $LiClO_4$ and LiTFSI were dried by heating under vacuum at 160 °C for 24 h. 12-Carat white gold leaf (Au:Ag 50:50, m/m), the precursor used to prepare the nanoporous gold (NPG) electrode, was purchased from Noris Blattgold GmbH, Germany. Super P carbon black was obtained from Timcal.

Methods.

Newly polished lithium metal foils (0.38 mm thick from Aldrich) were kept in 0.1 M $LiClO_4$-propylene carbonate (PC) electrolyte for at least 3 days before being used as the anode in a Li-O_2 cell containing a 0.1 M $LiClO_4$-DMSO electrolyte. This procedure was found to be effective in stabilizing the lithium metal, permitting cycling in DMSO. Before transferring to the cell containing the DMSO electrolyte, the lithium metal was rinsed with DMSO to remove any residual PC.

NPG electrode foils were prepared by dealloying white gold leaf by floating it on a bath of concentrated nitric acid for 5 minutes, following a published procedure (34). This process resulted in a freestanding thin film of NPG. The NPG was dried by heating under vacuum at 150^{o}C overnight. Morphological characterization of NPG by transmission electron microscopy (TEM, Jeol JEM 2011) is shown in Fig. S9. The pore size of NPG is estimated to be 30-50 nm. The cell assembly was conducted in an Ar-

filled glovebox by successively stacking a lithium metal anode, a glass fiber separator (0.3 mm in thickness soaked with ~ 0.1 mL of electrolyte) and a NPG cathode (ranging in mass loading from 0.15 to 5.0 mg/cm^2) placed on a stainless steel mesh. To quantify the surface area of the NPG a piece of NPG was mounted on a gold foil (2.0 cm x 2.0 cm x 0.025 mm), and the active surface area was determined by potential scanning between 0.2 and 1.5 V vs. Ag/AgCl in 0.5 M H_2SO_4 according to an established procedure (35). The active area of the NPG cathode was 50 m^2/g.

Carbon electrodes composed of Super P:PTFE 8:2, m/m, were prepared by coating pastes composed of carbon, binder, and 2-propanol onto a stainless steel mesh current collector, the mass loading of carbon cathode is typically 1.5 mg/cm^2. The electrodes were vacuum-dried at 200 °C for 24 hours. Similarly, electrodes containing gold nanoparticles (Super P:PTFE:Au 8:1:1, m/m) were prepared by coating pastes composed of carbon, binder, gold nanoparticles, and 2-propanol onto a stainless steel mesh current collector. The electrodes were first dried at 80 °C for two hours, then vacuum-dried at 200 °C for 24 hours.

FTIR was carried out on a Nicolet 6700 spectrometer (Thermo Fisher Scientific) either in transmission with a CsI pellet or on an ATR unit in a N_2 filled glove box. For the *in situ* SERS the NPG coated gold foil working electrode was placed behind a 1 mm thick sapphire window using a spectroelectrochemical cell described previously (17). Electrochemical measurements were carried out at room temperature using an Autolab PG30 electrochemical workstation. The DEMS system (7, 12) was built in-house and guided by the requirement to quantify all the gases consumed and evolved during the entire discharge and charge cycle. It is based on a commercial quadrupole mass

spectrometer (Thermo Fischer) with turbomolecular pump (Pfeiffer Vacuum) that is backed by a dry scroll pump (Edwards) and leak inlet which samples from the purge gas stream. The cell is based on a customized Swagelok design with polished stainless steel current collectors and double PTFE ferrules to ensure tightness. The cell assembly is as described above. The cathode current collector is integrated with two glued PEEK capillary tubes as purge gas inlet and outlet. The headspace above the cathode is ca 400 μL. The purge gas system consists of a gas cylinder, a digital mass flow controller (Bronkhorst), PEEK or stainless steel capillary tubing, a high pressure 2-position 6-port GC valve that allows for transfer from the glovebox without air exposure (all Valco), a T-piece where the MS samples and an outlet check valve (Swagelok) with an additional capillary to avoid back diffusion. Tightness was checked by Helium leak testing by means of the MS. Purge gas flows were typically 0.3 mL/min. The setup was calibrated for Ar, O_2, CO_2, H_2, N_2 and H_2O using calibration mixtures in steps over the anticipated concentration ranges to capture nonlinearity and cross-sensitivity (0-10% Ar/O_2 in each other plus 0-10000ppm of the other gases). Detection limits are <1 ppm. For typical discharge/charge currents relative gas evolution corresponding to < 0.1 % of the O_2 consumed/evolved is readily detected. Ultrapure He was used for the background. All calibration and quantification was performed using in-house software. Two working modes of the DEMS setup are used: a) Ar as carrier gas is used for detection of all gases evolved on charging, and b) In order to quantify O_2 consumption on discharge whilst measuring any gases evolved a mixture of ca. 5 % Ar in O_2 is used as the carrier gas. Ar acts as tracer gas with known invariable flux. As in a) the measured concentrations allow calculation of the flux of each component.

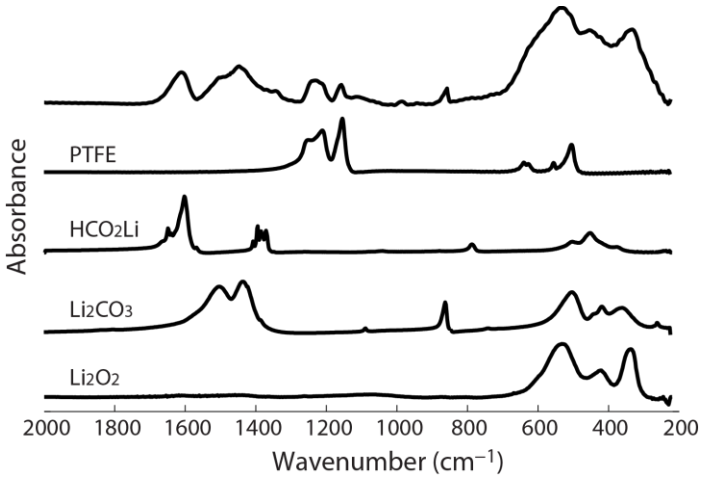

Fig. S1

FTIR data from a Super P carbon based cathode at the end of 1st discharge in 0.1 M $LiPF_6$-DME (dimethoxyethane) showing significant electrolyte decomposition. Such decomposition is not evident in powder X-ray diffraction due to poor crystallinity of the decomposition products, it is necessary to use techniques such as FTIR/NMR to observe the problems of ether electrolytes.

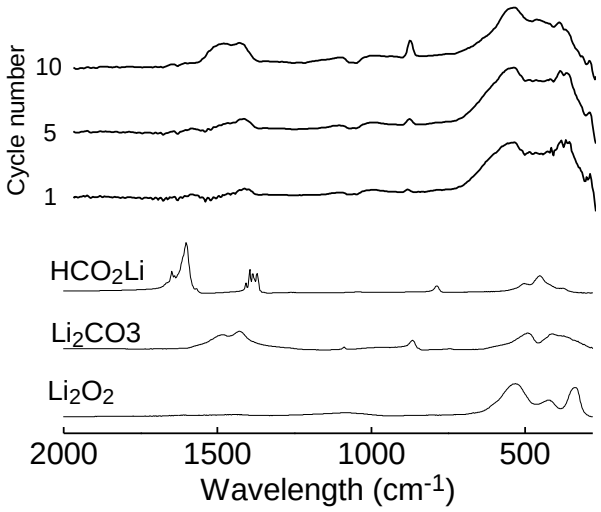

Fig. S2

FTIR spectra of a discharged NPG cathode in 0.1 $LiPF_6$-DME as function of cycle number, showing increasing growth of side-reaction products with cycling.

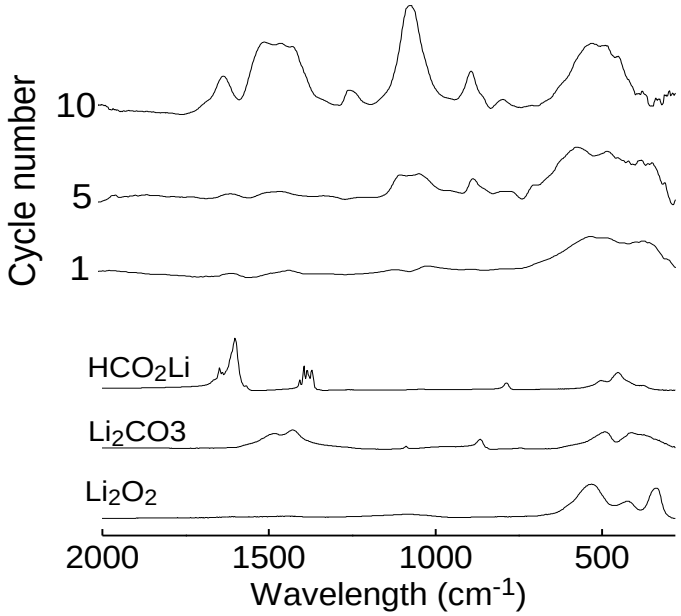

Fig. S3

FTIR spectra of a discharged NPG cathode in 0.1 $LiPF_6$-tetraglyme as function of cycle number. Bands are consistent with those observed for tetraglyme in ref 12.

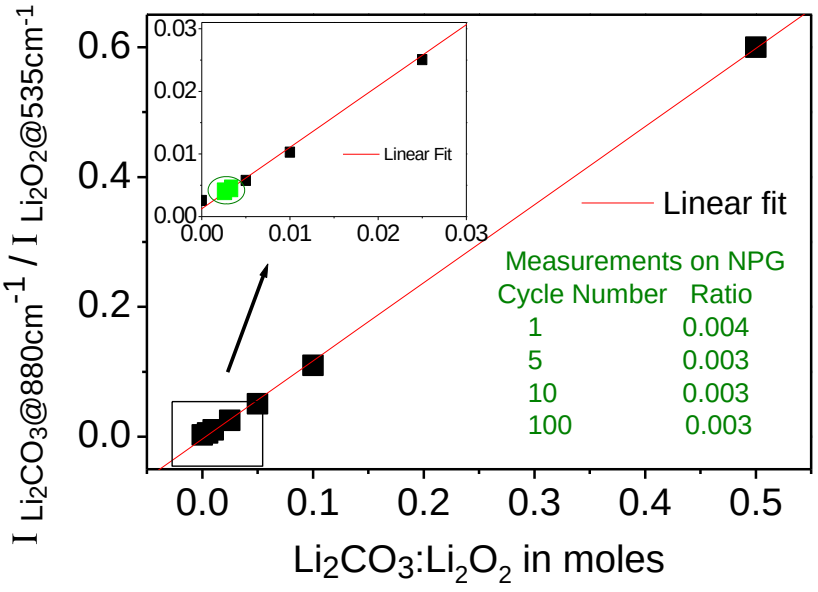

Fig. S4

FTIR calibration curve obtained by mixing known amounts of Li_2CO_3 and Li_2O_2 with different ratios. Note that the isolated Li_2CO_3 peak at 880 cm^{-1} was chosen in order to avoid interference from lithium formate. Inset shows expansion of the low ratio range. The green circle highlights the values obtained from the discharged NPG electrodes on different cycles.

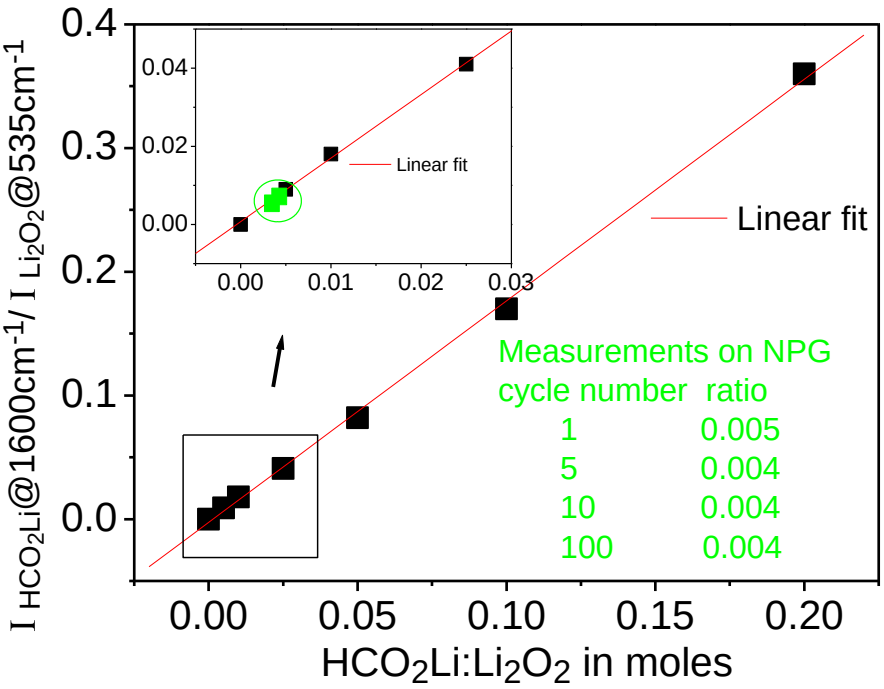

Fig. S5

FTIR calibration curve obtained by mixing known amounts of HCO_2Li and Li_2O_2 with different ratios. Note that the isolated HCO_2Li peak at 1600 cm^{-1} was chosen in order to avoid interference from lithium carbonate. Inset shows expansion of the low ratio range. The green circle highlights the values obtained from the discharged NPG electrodes on different cycles.

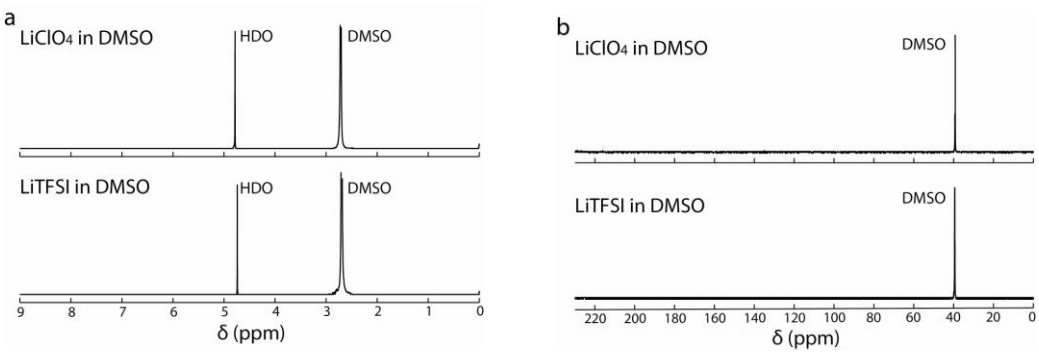

Fig. S6

(a) ^{1}H and (b) ^{13}C NMR data of 0.1 M $LiClO_4$-DMSO and LiTFSI-DMSO electrolytes used for a Li-O_2 cell with NPG cathode, after 100 discharge and charge cycles.

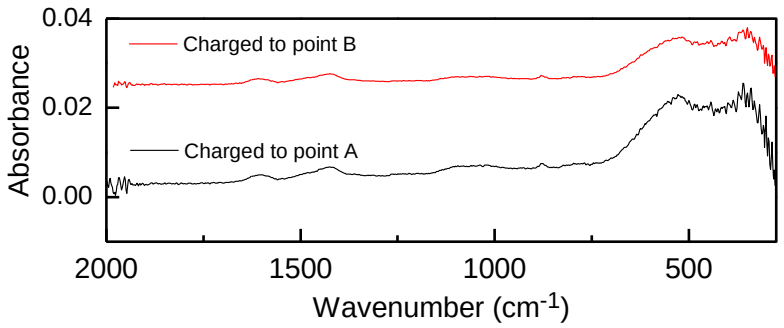

Fig. S7

FTIR spectra from a NPG electrode at the states of charge indicated by A and B in Fig. 1.

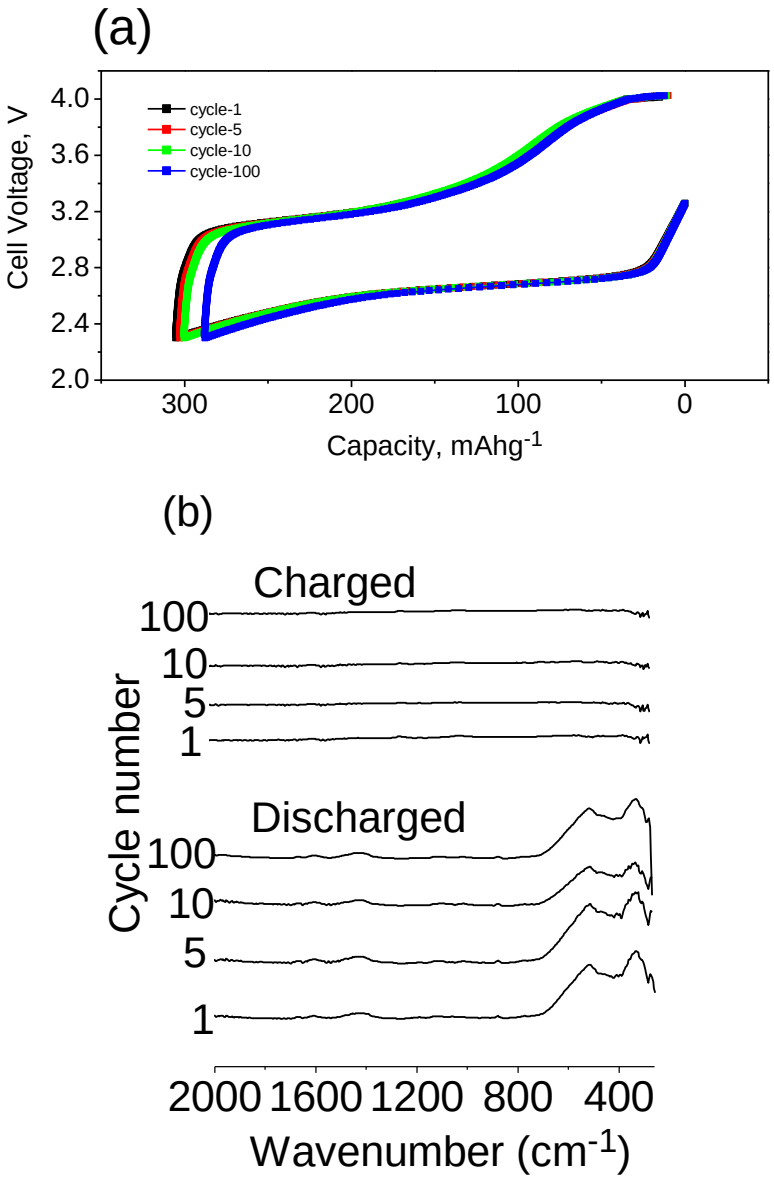

Fig. S8

(**a**) Discharge-charge curves of NPG cathode in oxygen saturated 0.1 M LiTFSI-DMSO electrolyte at a current density of 500 mAg^{-1}. (**b**) FTIR of NPG cathode as function of cycle number.

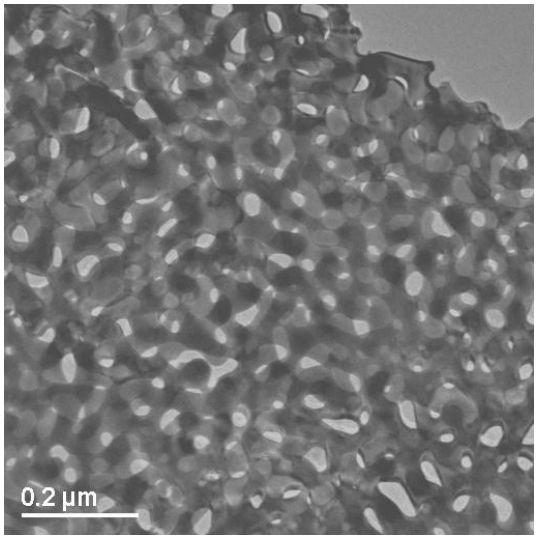

Fig. S9
TEM image of NPG.

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