

## Supporting Information

### A Lithium-Air Battery and Gas Handling System Demonstrator

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## Experimental

### Materials

Tetraethylene glycol dimethyl ether (tetraglyme,  $\geq 99\%$ , Sigma-Aldrich) was dried for 3 days over freshly activated molecular sieves (type 4 Å, Aldrich) before use. Lithium bis(trifluoromethane)sulfonimide (LiTFSI,  $\geq 99.95\%$ , Sigma-Aldrich) was dried at 120 °C overnight before use. Di-*tert*-butyl dibenzoquinone (DBBQ, 98%, Sigma-Aldrich) was dried under vacuum for 3 days before use. Karl-fischer titrations were performed to ensure water content of the electrolyte was  $< 10$  ppm. Compressed gases were all purchased from BOC. Activated carbon for the scrubber was purchased from Fluval. Molecular sieves (13X, 4-8 mesh) were purchased from Sigma-Aldrich. Cell components (lithium iron phosphate electrodes, glass fibre separators, Super P carbon electrodes and stainless-steel mesh) were dried at 120 °C before use. Cell housing components (current collector, PTFE gasket, flow field plate, bolts and screws) were dried in a vacuum oven at 70 °C for at least 3 hours before atmospheric transfer to the glovebox whilst hot. All materials and cell components were dried as described and stored in an Ar-filled glovebox ( $O_2$  and  $H_2O < 0.1$  ppm). All cells were configured in the Ar-filled glovebox ( $O_2$  and  $H_2O < 0.1$  ppm). Materials used for the construction of the gas handling rig were purchased from Swagelok (1/4" tubing, taps, back pressure regulator, fittings) Sigma-Aldrich (stainless steel gas bubbler) Omega Engineering (mass flow controllers, pressure transducers) and RS ( $CO_2$ /humidity sensor). The heated scrubber was made in-house by our workshops. The flow field plate for the cell was purchased from Fuel Cell Store.

## Flow Cell Measurements

Flow cells were assembled with 22 x 22 mm square lithium iron phosphate ( $\text{Li}_{1-x}\text{FePO}_4$ , LFP) negative electrodes, square 22 x 22 mm glass fibre separators, square 20 x 20 mm SuperP (SuperP:PTFE 80:20 wt%) electrode and square 20 x 20 mm stainless-steel mesh current collectors. Free standing SuperP electrodes were made by mixing SuperP and an aqueous PTFE suspension together (10 wt%) with isopropyl alcohol (IPA). IPA was added until a putty like consistency was achieved, after which the putty was subjected to calendaring from 1500  $\mu\text{m}$  down to 350  $\mu\text{m}$  in 100  $\mu\text{m}$  increments. 600  $\mu\text{L}$  of electrolyte (1M LiTFSI in tetraglyme, 50 mM DBBQ) was added to the cell. Eight bolts with wingnuts tightened to finger tightness were used to seal the cell and ensure sufficient stack pressure for discharge. Cells were discharged on a BioLogic SP-50 potentiostat and were allowed a 4 hour open circuit period at the same gas flowrate used for discharge before applying the relevant current density.

## $\text{Li}_2\text{O}_2$ yield measurements

The positive electrodes were extracted and washed with dimethoxyethane (DME). Yield measurements were performed using the previous reported method.<sup>1</sup> The were discharged at 20 °C at a current density of 0.5  $\text{mA cm}^{-2}$  to a capacity of 10 mAh (100%  $\text{O}_2$ ) or 5 mAh (20%  $\text{O}_2/\text{air}$ ). The discharged electrodes and separators were added to a vial containing a 3 mL of  $\text{H}_2\text{O}$ . A ten times dilution was then carried out (five for 20%  $\text{O}_2/\text{air}$ ). The resulting solution was added to an equal volume of  $\text{TiOSO}_4$  (2 wt.%) in 1 M  $\text{H}_2\text{SO}_4$  ( $\text{H}_2\text{O}$ ). The  $\lambda_{\text{max}}$  at 405 nm (Ocean Optics USB2000+ fiber optic spectrometer) were compared to a calibration curve, which was obtained by using known standards of  $\text{H}_2\text{O}_2$ .

## SEM Imaging

The positive electrodes were extracted and washed with dimethoxyethane (DME) before air-free transfer to the scanning electron microscope (SEM). Imaging was performed on a FEI Quanta200 3D FIB-SEM (FEI, United States of America) and a Zeiss Crossbeam550 FIB-SEM (Carl Zeiss, Germany) at accelerating voltages of 5.00 kV.

## FT-IR

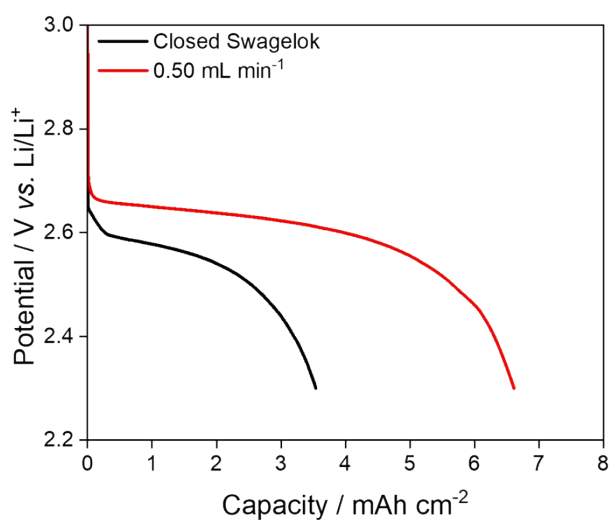
Fourier transform infra-red (FTIR) spectra were recorded on a Bruker Alpha II spectrometer with a Pt ATR module in a  $\text{N}_2$ -filled glovebox, without further manipulation of the dried electrode.

## Calculation of Normalised Flowrate

Normalised flowrates based on oxygen consumption were calculated as follows:

$$\frac{Q_{min}}{nF} = mol\ min^{-1}$$

Where  $Q_{min}$  is the charged passed per minute,  $n$  is the number of electrons and  $F$  is the Faraday constant. The ideal gas equation was then used to calculate volumes, with 1000 mbar assumed pressure.



**Figure S1.** Discharge profiles of cells discharged in a static configuration (Swagelok, 177  $\mu\text{L cm}^{-2}$  electrolyte) and of the demonstrator cell under a flow of 100%  $\text{O}_2$  (0.50  $\text{ml min}^{-1}$ ). For both cells the electrolyte was 1M LiTFSI dissolved in tetraglyme with 50 mM DBBQ.

**Table S1.** % $\text{Li}_2\text{O}_2$  yields of cells run under the flow of different gas compositions, discharged at a current density of 0.5  $\text{mA cm}^{-2}$ .

Cell	% $\text{Li}_2\text{O}_2$ Yield
100% $\text{O}_2$	82
20% $\text{O}_2$	62
Compressed Air	52
Scrubbed Air	48

**Table S2.** Discharge voltages of the cells from Figure 3. Voltages taken at 50% of discharge.

Flow Rate / mL min <sup>-1</sup>	100% O <sub>2</sub> / V vs. Li/Li <sup>+</sup>	20% O <sub>2</sub> / V vs. Li/Li <sup>+</sup>	Air / V vs. Li/Li <sup>+</sup>
0.05	2.48		
0.1	2.54	2.47	2.54
0.25	2.54	2.57	2.57
0.5	2.62	2.54	2.56
0.75		2.55	2.58
2.5		2.57	2.57
5		2.59	2.48

**Table S3.** Normalised flow rates based on the applied current densities and oxygen consumption with the Li-air demonstrator.

	100% O <sub>2</sub> / mL min <sup>-1</sup>	20% O <sub>2</sub> / mL min <sup>-1</sup>	Air (21% O <sub>2</sub> ) / mL min <sup>-1</sup>
<b>0.1 mA cm<sup>-2</sup> (0.4 mA)</b>	0.003	0.015	0.014
<b>0.5 mA cm<sup>-2</sup> (2 mA)</b>	0.015	0.075	0.071

<b>Performance</b>		<b>Cathode</b>	
Specific capacity (mAh g <sup>-1</sup> )	352	Volume fractions	
Specific energy (Wh kg <sup>-1</sup> )	934	Carbon (%)	20.4
Pack Specific energy (Wh kg <sup>-1</sup> )	587	Electrolyte (%)	27.5
<b>System specific energy (Wh kg<sup>-1</sup>)</b>	<b>454</b>	Binder (%)	13.6
Volumetric capacity – (mAh cm <sup>-3</sup> )	491	Li <sub>2</sub> O <sub>2</sub> (%)	38.5
Volumetric energy density (Wh L <sup>-1</sup> )	1312	Total areal weight - (g cm <sup>-2</sup> )	6.0 x 10 <sup>-2</sup>
Pack volumetric energy (Wh L <sup>-1</sup> )	571	Total areal volume (cm <sup>3</sup> per cm <sup>2</sup> )	3.0 x 10 <sup>-2</sup>
<b>System volumetric energy density (Wh L<sup>-1</sup>)</b>	<b>444</b>	Cathode thickness - (μm)	300
<b>Electrochemical variables</b>		Areal capacity Li <sub>2</sub> O <sub>2</sub> (mAh cm <sup>-2</sup> )	31
Voltage (vs Li <sup>+</sup> /Li)	2.6	Specific capacity (mAh g <sup>-1</sup> )	521
<b>Pack and power</b>		<b>Ceramic protected lithium Anode</b>	
Pack energy (kWh)	100	Li thickness (μm)	191
Pack specific energy (Wh kg <sup>-1</sup> )	587	Lithium excess (%)	20
Pack volumetric energy (Wh L <sup>-1</sup> )	571	Ceramic thickness (μm)	10
Pack mass scaling factor	1.6	Current collector thickness (μm)	20
Pack volume scaling factor	2	Saving factor due to bipolar	2
Pack mass (kg)	170	Density - (g cm <sup>-3</sup> )	5.1
Pack volume (L)	175	Areal mass - (g cm <sup>-2</sup> )	1.8 x 10 <sup>-3</sup>
		Areal volume (cm <sup>3</sup> per cm <sup>2</sup> )	1.0 x 10 <sup>-3</sup>
		<b>Current collector/flow field</b>	
Bilayer thickness (cm)	5.4 x 10 <sup>-2</sup>	CC density (g cm <sup>-3</sup> )	2.7
Cell dimension (cm)	30	Thickness μm	40
Current density (mA)	1	Areal weight (g cm <sup>-2</sup> )	8.3 x 10 <sup>-3</sup>
Additional volume (%) for volume change	15	Areal volume - (cm <sup>3</sup> per cm <sup>2</sup> )	3.1 x 10 <sup>-3</sup>
Energy per cell (Wh)	63	Saving factor due to bipolar	1.3
Total cells	1579	<b>Polypropylene Separator</b>	
Length of pack (cm)	85	CC density (g cm <sup>-3</sup> )	0.50
Current per cell (mA)	900	Thickness (μm)	25
Power per cell (W)	2.4	Areal weight (g cm <sup>-2</sup> )	1.2 x 10 <sup>-3</sup>
Total power (kW)	3.8	Areal volume - (cm <sup>3</sup> per cm <sup>2</sup> )	2.5 x 10 <sup>-3</sup>
<b>Balance of Plant</b>		<b>Additional Electrolyte in Separator</b>	
BOP volume (L)	50	Solvent density (g cm <sup>-3</sup> )	1
BOP mass (kg)	50	Porosity of separator (%)	55
System volume (L)	225	Thickness (μm)	25
System mass (kg)	220	Areal weight (g cm <sup>-2</sup> )	1.4 x 10 <sup>-3</sup>
Volumetric energy density (Wh L <sup>-1</sup> system)	444	Areal volume - (cm <sup>3</sup> per cm <sup>2</sup> )	2.5 x 10 <sup>-3</sup>
Specific energy (Wh kg <sup>-1</sup> system)	454		

**Table S4.** Parameters used to develop system performance predictions of an open Li-air system.

## References

1. P. Hartmann, C. L. Bender, J. Sann, A. K. Dürr, M. Jansen, J. Janek and P. Adelhelm, *Phys. Chem. Chem. Phys.*, 2013, **15**, 11661–11672.