

Electronic Supplementary Information (ESI)

**The discharge rate capability of rechargeable Li-O<sub>2</sub> batteries**

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### 1. Rate capability - specific capacity normalized by discharged electrode weight

The discharged electrode weight (carbon + catalyst + binder + **discharge products**) was used to normalize the discharge capacity of all Li-O<sub>2</sub> cells **assuming that all the charge is associated with Li<sub>2</sub>O<sub>2</sub> formation**. The mass of Li<sub>2</sub>O<sub>2</sub> formed for each cell was obtained by converting the discharge capacity (C) to the weight of Li<sub>2</sub>O<sub>2</sub> via the following equation

$$\text{weight of Li}_2\text{O}_2 \text{ (g)} = \frac{\text{M.W.}_{\text{Li}_2\text{O}_2} \text{ (g/mol)} \cdot \text{discharge capacity (C)}}{n \cdot F \text{ (C/mol)}}$$

, where M.W.Li<sub>2</sub>O<sub>2</sub> is the molecular weight of Li<sub>2</sub>O<sub>2</sub> (45.882 g/mol), n is the numbers of electron transferred of discharge reaction assuming final product as Li<sub>2</sub>O<sub>2</sub> (n = 2), F is Faraday constant (96485 C/mol).

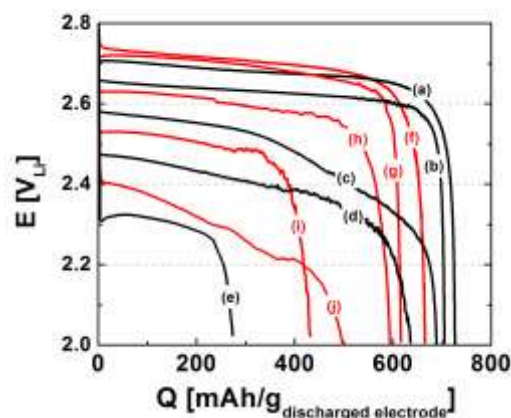


Fig. S1 Discharge profiles of Li-O<sub>2</sub> single cells of pure Vulcan (a)-(e) and Au/C. The discharge rate is 100 mA/g<sub>carbon</sub> for (a) and (f), 250 mA/g<sub>carbon</sub> for (b) and (g), 500 mA/g<sub>carbon</sub> for (c) and (h), 1000 mA/g<sub>carbon</sub> for (d) and (i), and 2000 mA/g<sub>carbon</sub> for (e) and (j).

## 2. Transport properties estimation in selected electrolytes

Symbols:

D: Diffusion coefficient

t: Transference number

$\eta$ : viscosity of solvent

T: temperature

$C_o$ : solubility of oxygen

$\alpha$ : Bunsen coefficient of Oxygen in the electrolyte

Stokes-Einstein diffusion equation

$$D = \frac{k_B T}{6\pi\eta a} \text{ where the hydrodynamic radius } a = 121 \text{ pm for oxygen}$$

Ionic diffusion equation

$$D_{Li^+} = \frac{\sigma_{Li^+} RT}{z^2 F^2 [Li^+]} t_{Li^+} \text{ where } z = 1 \text{ for lithium cations}$$

For the binary ionic salts used in lithium-based electrolytes, lithium ion transference number is calculated as follows:

$$t_{Li^+} = \frac{D_{Li^+}}{D_{Li^+} + D_-}$$

1) Species transport in 0.1 M  $Li^+$  in pure DME

- Oxygen diffusion coefficient<sup>1,2</sup>

$$\eta = 4.5 \cdot 10^{-4} \text{ Pa} / \text{s} \Rightarrow D_{O_2} \approx 4.0 \cdot 10^{-5} \text{ cm}^2 \text{s}^{-1}$$

- Solubility of Oxygen<sup>3</sup>

$$\alpha_{DME} = 0.2143 L_{O_2} / L_{DME} \Rightarrow C_o = 0.00876 M$$

- Lithium transference number<sup>4</sup>

$$\text{In } 0.1 \text{ M LiCF}_3\text{SO}_3/\text{DME}, D_{Li^+} \approx D_{CF_3SO_3^-} \approx 13.3 \cdot 10^{-6} \text{ cm}^2 \text{s}^{-1} \Rightarrow t_{Li^+} \approx 0.5$$

This calculated value of transference number agrees well with the value of 0.43 reported in 0.01 M  $LiClO_4$  in PC/DME by Makoto et al.<sup>5</sup>

- Lithium diffusion<sup>4,2</sup>

$$\text{In } 0.1 \text{ M LiCF}_3\text{SO}_3/\text{DME}, D_{Li^+} \approx 13.3 \cdot 10^{-6} \text{ cm}^2 \text{s}^{-1}$$

$$D_{Li^+} \approx 7.3 \cdot 10^{-6} \text{ cm}^2 \text{s}^{-1} \text{ in } \sim 0.5 \text{ M LiTFSI/DME at } 30^\circ\text{C}$$

2) Species transport in 1 M in PC/DME (1:2)

- Oxygen diffusion coefficient

$$\eta = 1.98 \cdot 10^{-3} \text{ Pa} / \text{s} \Rightarrow D_{O_2} \approx 9 \cdot 10^{-6} \text{ cm}^2 \text{s}^{-1}$$

- Solubility of Oxygen<sup>3</sup>

$$\alpha_{PC/DME} = 0.0998L_{O_2} / L_{PC/DME} \Rightarrow C_o = 0.0041M$$

- Lithium transference number<sup>2</sup>

A mixture of PC and DME (1:2) by volume corresponds to a molar ratio of ~40% PC in DME. This value is used to read needed data in fig. 2 of the work of Hayamizu et al.

In ~0.5 M LiTFSI/DME,  $D_{Li^+} \approx 5 \cdot 10^{-6} cm^2 s^{-1}$ ,  $D_{TFSI} \approx 6.5 \cdot 10^{-6} cm^2 s^{-1} \Rightarrow t_{Li^+} \approx 0.43$

As a first order approximation, the lithium transference number is assumed to vary very little from 0.5 M to 1 M Li<sup>+</sup> in PC/DME.

- Lithium diffusion<sup>6</sup>

By approximating the transference number of lithium in PC/DME to 0.4, the diffusion coefficient of lithium is calculated from data provided by Yoshio et al.<sup>6</sup>

In 1 M LiBF<sub>4</sub> in PC/DME (1:2),  $\sigma \approx 7.2 \cdot 10^{-3} S \cdot cm^{-1} \Rightarrow D_{Li^+} \approx 7.7 \cdot 10^{-7} cm^2 s^{-1}$

### 3) Species Transport in 1 M in pure PC

- Oxygen diffusion coefficient<sup>3</sup>

$$\eta = 8.06 \cdot 10^{-3} Pa / s \Rightarrow D_{O_2} \approx 2.2 \cdot 10^{-6} cm^2 s^{-1}$$

- Solubility of Oxygen<sup>3</sup>

$$\alpha_{PC} = 0.0516L_{O_2} / L_{PC} \Rightarrow C_o = 0.0021M$$

- Lithium transference number<sup>2</sup>

In ~0.5 M LiTFSI/PC,  $D_{Li^+} \approx 1.6 \cdot 10^{-6} cm^2 s^{-1}$ ,  $D_{TFSI} \approx 2.8 \cdot 10^{-6} cm^2 s^{-1} \Rightarrow t_{Li^+} \approx 0.35$

As a first order approximation, the lithium transference number is assumed to be fixed from 0.5 M to 1 M Li<sup>+</sup> in PC.

- Lithium diffusion<sup>6</sup>

By approximating the transference number of lithium in pure PC to 0.35, the diffusion coefficient of lithium is calculated from data provided by Yoshio et al.

In 1 M LiBF<sub>4</sub>/PC,  $\sigma \approx 2.8 \cdot 10^{-3} S \cdot cm^{-1} \Rightarrow D_{Li^+} \approx 3 \cdot 10^{-7} cm^2 s^{-1}$

### 3. Transport characteristics in the O<sub>2</sub> electrodes used in our experiments

#### 3-a. Limiting fluxes of O<sub>2</sub> and Li<sup>+</sup> within the porous cathode in 0.1 M Li<sup>+</sup> DME electrolyte

##### Symbols:

J: Flux of the species

D = Diffusion coefficient of the species

C(x), C<sub>o</sub>: Concentration and soluble concentration of species in the media

n: Number of Electron transferred

j: Electrode-area normalized current density

D<sub>eff</sub>: Effective diffusion coefficient in the flooded-porous electrode

β<sub>O<sub>2</sub></sub>: Bruggeman constant of oxygen in the porous cathode

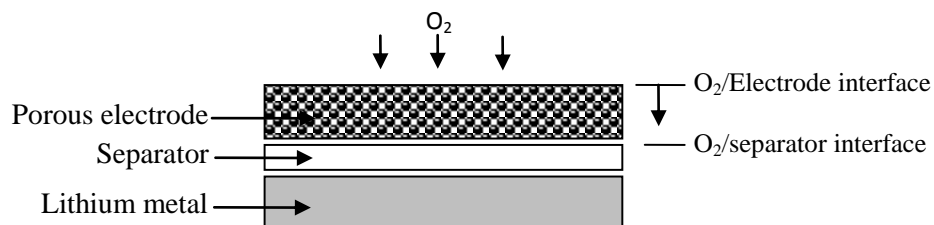
$$J_{\text{lim}} = D \cdot \varepsilon^{\beta-1} \cdot \frac{C_o}{t} \text{ where } \beta \text{ is equal to 3 for oxygen and 2.5 for Li}^+.$$

$$J_{\text{lim}_{\text{O}_2}} = (4 \cdot 10^{-5} \text{ cm}^2 / \text{s}) \cdot (0.73)^{3-1} \cdot \frac{0.00876 \cdot 10^{-3} \text{ mol}_{\text{O}_2} / \text{cm}^3}{20 \cdot 10^{-4} \text{ cm}} \approx 9 \cdot 10^{-8} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$$

$$J_{\text{lim}_{\text{Li}^+}} = (10 \cdot 10^{-6} \text{ cm}^2 / \text{s}) \cdot (0.73)^{2.5-1} \cdot \frac{0.1 \cdot 10^{-3} \text{ mol}_{\text{O}_2} / \text{cm}^3}{20 \cdot 10^{-4} \text{ cm}} \approx 3 \cdot 10^{-7} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$$

In the calculation of limiting flux of Li<sup>+</sup>, an average value of the reported diffusion coefficients is used. The diffusion coefficient values vary from 7\*10<sup>-6</sup> cm<sup>2</sup>.s<sup>-1</sup> to 13\*10<sup>-6</sup> cm<sup>2</sup>.s<sup>-1</sup> depending on the lithium salt in the electrolyte as exemplified in ESI section 2.

#### 3-b. Concentration of O<sub>2</sub> in the flooded electrode: simplified model



The arrow indicates the distance into the electrode

The Bruggeman relation applied to the diffusion of oxygen in the porous, flooded oxygen electrode states<sup>7</sup>,

$$D_{\text{eff}} = D \cdot \varepsilon^{\beta_{\text{O}_2}-1} \text{ with } \beta_{\text{O}_2} = 3$$

A combination of Fick's diffusion law and electrochemical conversion of oxygen yields the following equation for the O<sub>2</sub>-concentration from the entrance of the porous electrode (x=0) to the electrode/separator interface (x = L).

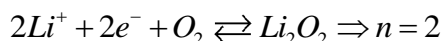
$$C(x) = C_o \exp\left(-x \sqrt{\frac{k}{D_{eff}}}\right)$$

$$J = -D \frac{\partial C(x)}{\partial x} \Rightarrow J(x=0) = C_o \sqrt{kD_{eff}}$$

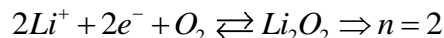
$$J = \frac{j}{nF}$$

$$k = \frac{j^2}{n^2 F^2 C_o^2 D_{eff}}$$

$$\frac{C(x)}{C_o} = \exp\left(-x \frac{j}{nFC_o D_{eff}}\right)$$



### 3-c. Oxygen consumption at the O<sub>2</sub> electrode



$$M_{O_2} = 32 g_{O_2} / mol_{O_2}$$

$$C(mol_{O_2} / mAh) = \frac{1}{2\left(\frac{mol_{e^-}}{mol_{O_2}}\right)F\left(\frac{C}{mol_{e^-}}\right)} (3.6 C / mAh) = 1.9 \cdot 10^{-5} mol_{O_2} / mAh$$

Assuming Oxygen is an ideal gas at 1atm and 25°C during the cell testing,

$$\bar{V}_{O_2} (L / mol_{O_2}) = 22.465 L / mol_{O_2}$$

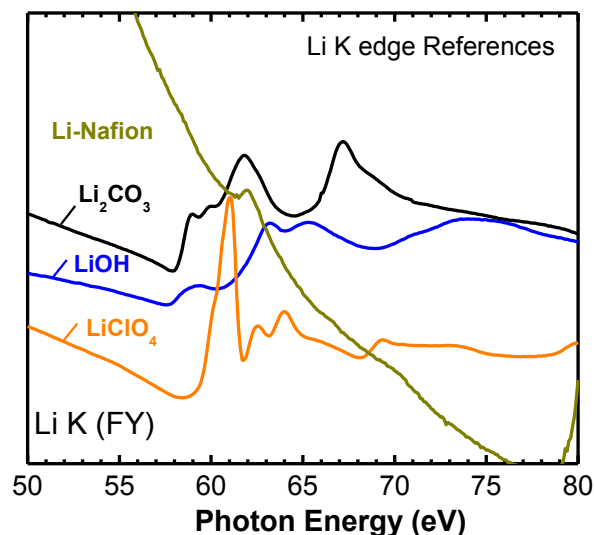
Henceforth,

$$\bar{C}(mL_{O_2} / mAh) = 0.419 mL_{O_2} / mAh$$

The maximum capacities achieved for the cells in the present publication is ~3500 mAh/g<sub>carbon</sub> for an average carbon content of 0.5 mg in all electrodes. This corresponds to a maximum total

discharge of 1.75 mAh and 0.73 mL of oxygen consumed. Consequently, all cells tested contained at least 340 times more oxygen than required (250 mL oxygen tank); the pressure drop from oxygen consumption by the cell was negligible.

#### 4. Li-K edge X-ray absorption near edge structure spectra of reference compounds



**Fig S2** Li K edge XANES spectra of reference compounds: Li-Nafion,  $\text{Li}_2\text{CO}_3$ ,  $\text{LiOH}$ , and  $\text{LiClO}_4$ .

Reference:

1. M. Saleh, S. Akhtar, M.S Ahmed, *Phys. Chem. Liq.* 2008, **46**, 140-153.
2. K. Hayamizu, Y. Aihara, *Electrochimica Acta*, 2004, **49**, 3397-3402.
3. J. Read, K. Mutolo, et al., *J. Electrochem. Soc.*, 2003, **150**, A1351-A1356
4. Y. Saito, H. Yamamoto, H. Kageyama, O. Nakamura, *J. Materials Science*, 2000, **35**, 809-812.
5. M. Ue, S. Mori, *J. Electrochem. Soc.*, 1995, 142, 2577.
6. M. Yoshio, H. Nakamura, M. Hyakutake, S. Nishikawa, K. Yoshizuka, *J. Power Sources*, 1993, **41**, 77-86.
7. P. Andrei, J.P. Zheng, M. Hendrickson, E.J. Plichta, *J. Electrochem. Soc.*, 2010, **157**, A1287-A1295.
8. Y.-C. Lu, H. A. Gasteiger, M. C. Parent, V. Chiloyan and Y. Shao-Horn, *Electrochem. Solid State Lett.*, 2010, 13, A69-A72.