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Additional graphs:



**Figure S1.** Galvanostatic cycling of Na-O<sub>2</sub> cells at 200 mA g<sup>-1</sup>. (-) 10 mM EtV(OTf)<sub>2</sub>, 250 mM NaOTf, diglyme. (-) 250 mM NaOTf, diglyme.



**Figure S2.** Cyclic voltammetry data collected on a 3 mm ø glassy carbon electrode at 20 mV s<sup>-1</sup>. (-) 10 mM EtV(OTf)<sub>2</sub>, 250 mM NaOTf, diglyme under Ar, (-) 10 mM EtV(OTf)<sub>2</sub>, 250 mM NaOTf, diglyme under O<sub>2</sub>, (-) 250 mM NaOTf, diglyme under O<sub>2</sub>.

## **Experimental details**

### **Electrochemical measurements**

1 inch Swagelok cells (figure S3) were utilized for electrochemical experiments. The working electrode was made of an acetylene black carbon (50 % compressed, Chevron) with Nafion binder (20% wt solution in Alcohol/water mix, Aldrich) ink (2:1 carbon:binder) coated onto Celgard (2320) with a loading of 0.8 mg cm<sup>-2</sup> (+/- 0.05 mg cm<sup>-2</sup>). Capacities have been normalized to the mass of carbon in the working electrode. 1 inch electrodes were then punched from this and dried under vacuum for 24 h at room temperature before being transferred to an argon filled glovebox. The counter/reference electrode was a 1 inch sodium metal disc. Discs were cut from sodium metal cubes (99.9%, Sigma-Aldrich) that had been pressed in order to remove the passivating oxide layer from the faces of the cube. 1 inch sodium beta-alumina discs (25.4 mm Ø x 1 mm, lonotec) were used as sodium conductive membranes to separate the working electrode from the counter/reference electrode and thus prevent the mass transport of ethyl viologen to the sodium electrode. The electrolyte used was 250 mM NaOTf (sodium triflate, 98%, Sigma-Aldrich) in diglyme (Hi-Dry, Romil), with and without 10 mM ethyl viologen trifilate, EtV(OTf)<sub>2</sub>. Prior to use, the electrolyte was dried using 3 Å type molecular sieves (Sigma-Aldrich) for at least 24h prior to use. The EtV(OTf)<sub>2</sub> was prepared in house from EtVI<sub>2</sub> according to ref.<sup>1</sup> Prior to use, NaOTf and EtV(OTf)<sub>2</sub> were dried under vacuum at 120 °C for 24 hours. Cell assembly and electrolyte preparation was done inside an argon filled glovebox (< 1 ppm water content, < 10 ppm oxygen content, M-Braun). The water content in the electrolytes was < 20 ppm (Mettler–Toledo Karl Fischer titration).

The cells were assembled as follows. First, a 1 inch sodium metal electrode was placed. Then, a 1 inch Celgard separator (2320) wetted with 50  $\mu$ L of electrolyte (250 mM NaOTf in diglyeme) was placed, followed by a 1 inch sodium beta-alumina discs, followed by a 1 inch Celgard separator (2320) wetted with 50  $\mu$ L of electrolyte containing 10 mM EtV(OTf)<sub>2</sub>. After that, the carbon working electrode was placed and a further 100  $\mu$ L of electrolyte containing 10 mM EtV(OTf)<sub>2</sub> was added. Finally, a stainless steel spacer and stainless steel piston with holes were placed on top of the working electrode, as illustrated in figure S3.

Full reduction of all the  $EtV^{2+}$  present in the cells to  $EtV^+$  would result in a capacity of ca 10 mAh/g (normalized by the mass of carbon), which is much smaller than the total capacity observed in the mediated Na-O<sub>2</sub> cell (see figure 1A).



Figure S3. Diagram of the Swagelok cells used for electrochemical measurements.

Electrochemical measurements were performed using a Princeton Applied Research variable multichannel potentiostat (VMP2). Pressure change measurements were used to determine the number of moles of oxygen consumed during galvanostatic discharges. Cell pressure data was collected using a pressure sensor supplied by EL-Cell, which was connected to the Swagelok cell. Prior to carrying out electrochemical cycling in oxygen cells were purged with oxygen at 1.7 bar for 30s. Cells were then left at OCV for 2 h before cycling.

Cyclic voltammetry (CV) experiments were performed using a U-cell containing two glass compartments separated by a glass frit. A glassy carbon electrode and Na foil pressed onto a stainless steel mesh were used as the oxygen (working) electrode and sodium (counter and reference) electrode, respectively. Viologen containing electrolyte was used in the working electrode compartment while mediator-free electrolyte was used in the sodium electrode compartment. Oxygen was bubbled through the working electrode electrolyte for 10 minutes to produce a saturated solution. CVs were performed at a scan rate of 10 mV s<sup>-1</sup> between 1.5 and 4.2 V.

# O<sub>2</sub> consumption analysis

The evaluation of the number of moles of oxygen consumed during discharge from pressure change measurements was done as follows. First, the internal volume of Swagelok cells were determined using a pressure gauge with a known internal volume of 3 ml. The Swagelok cells were connected to the pressure gauge using Swagelok connections and PEEK tubing, with a Swagelok needle valve used to isolate each system. The pressure of gas in the pressure gauge was set to 1.7 bar, while the pressure in the Swagelok cell was set between 1 - 1.7 bar. Upon opening the needle valve connecting the Swagelok cell to the pressure gauge, the pressure of the system equilibrated. By rearranging equation 1 it was then possible to determine the volume of the Swagelok cells.

$$P_{cell}V_{cell} + P_GV_G = P_{tot}(V_{cell} + V_G)$$

Equation 1

where  $P_{cell}$  and  $P_{G}$  are the pressure values within the cell and the pressure gauge, respectively, before equilibration,  $P_{tot}$  is the total pressure in the system after opening the needle value, and  $V_{cell}$  and  $V_{G}$  are the volumes of the cell and the pressure gauge, respectively.

Once the internal volume of the cell has been determined (which varied between 6-8 ml), it is possible to determine the number of moles of oxygen consumed during discharge from the change in pressure in the system by using gas law:

$$PV = nRT$$
 Equation 2

where P is the pressure in the system (bar), V is the internal volume of the system (L), n is the number of moles (mol), R is the ideal gas constant (0.08314 bar L  $K^{-1}$  mol<sup>-1</sup>) and T is the temperature in K.

The small differences in the amount of oxygen consumed in mediated and unmediated  $Na-O_2$  cells (Figure 1B) are within the uncertainty of these measurements.

## Ex-situ electrode characterization

Following discharge cells were transferred into an argon filled glovebox and disassembled. The working electrode was then rinsed with diglyme and dried. Once dried the electrode was subjected to ex-situ measurements.

Ex-situ XRD measurements were performed in transmission mode on a Rigaku smartlab. An airtight sample holder (Bruker) was employed to prevent the degradation of the discharge product.

Ex-situ Raman measurements were recorded using a Renishaw inVia confocal Raman microscope with a 785 nm laser. To prevent heat damage to the celgard on which the electrode was coated the laser power was reduced to 0.1 %. Spectra were recorded using a 10s acquisition time over 5 acquisitions. To prevent the degradation of the discharge product a sealed cell, maintaining an argon atmosphere, with a quartz window was used.

SEM images were recorded using a XL30SEM. During transport from the glovebox to the SEM room samples were double bagged in grip seal bags under an argon atmosphere. Transfer from the glovebox room to the SEM room took two minutes. Transfer from the grip seal bag to the SEM took between 5-10 s during which time samples were exposed to ambient conditions.



Figure S4. SEM image of electrode discharged in the absence of EtV<sup>2+</sup>.



Figure S5. SEM image of electrode discharged in the presence of  $EtV^{2\ast}.$ 



Figure S6. SEM image of electrode discharged in the presence of EtV<sup>2+</sup>.

#### **UV-Vis titrations**

Solutions of 2 mM EtV(OTf)<sub>2</sub>, 250 mM NaOTf in MeCN (Acetonitrile, anhydrous, 99.8%, Sigma-Aldrich) were prepared in an argon filled glovebox. This solution was then reacted with 1.8 moles equivalent of lithiated lithium titanium oxide (LLTO, prepared in house according to <sup>2</sup>) for one hour. The resulting solution was filtered through a PTFE filter (Thermo Scientific), this resulted in a blue solution of EtV<sup>+</sup>. To this solution aliquots of oxygen saturated (8 mM O<sub>2</sub>) 250 mM NaOTf in MeCN electrolyte were added such that the number of moles of oxygen in each aliquot was equal to  $1/5^{th}$  the number of moles of EtV<sup>+</sup> initially present in the solution.

A sample of the EtV<sup>+/2+</sup> solution was taken at each step in the process and diluted down 25x with 250 mM NaOTf in MeCN. The absorbance of these solutions were then recorded using a Lambda Bio XLS UV-Vis spectrometer.

Since each oxygen aliquot is expected to oxidize 20% of  $EtV^+$  in solution, it is expected that each aliquot will reduce the intensity of the  $EtV^+$  UV-vis bands by 20%. This is confirmed in figure S4, where the fit of the experimental data gives a slope close to -1/5 = -0.2.



Figure S7. Change in absorbance at 606 nm with the addition of aliquots of oxygenated electrolyte.

#### References

<sup>1</sup> M. J. Lacey, J. T. Frith, and J. R. Owen, *Electrochem. Commun.*, **26**, 74–76, (2013).

<sup>2</sup> L. Yang, J. T. Frith, N. Garcia-Araez, and J. R. Owen, Chem. Commun., 51, 1705–1708, (2014).