Electronic Supplementary Material (ESI) for Energy & Environmental Science

Supporting Information for

Lithium and Oxygen Vacancies and their Role in Li_2O_2 Charge Transport in Li-O_2 Batteries

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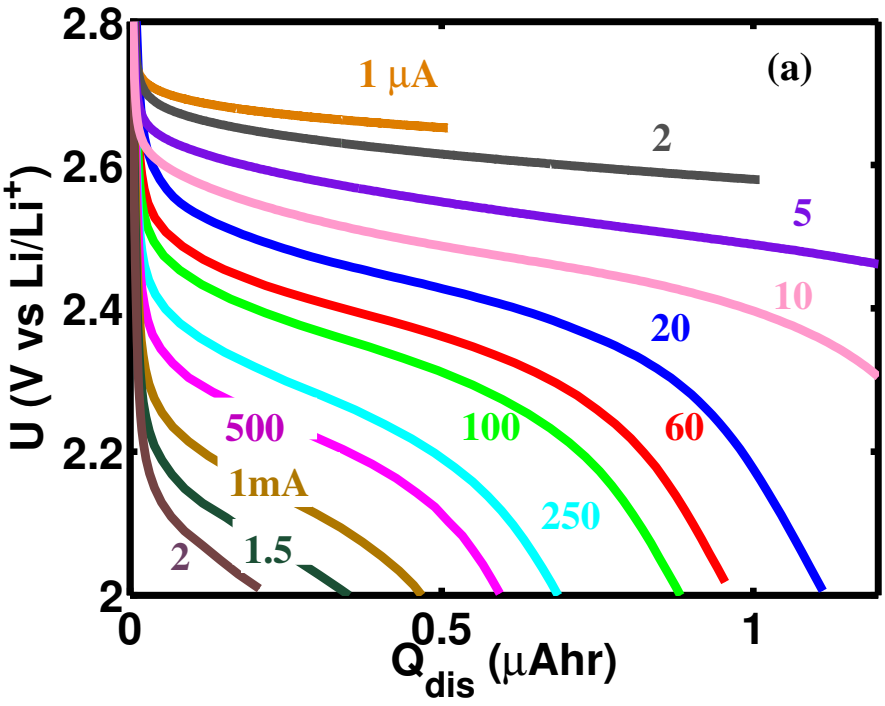

Figure S1. Experimental Li–O_2 galvanostatic discharge curves (U versus Q_{dis}) observed in a bulk electrolysis cell on a ~1 cm^2 area glassy carbon (GC) cathode with 1 M LiTFSI in DME as the electrolyte, ~1 bar O_2 pressure, and at T = 30 °C. The various curves for different discharge currents (1–500 μA and 1–2 mA) are labeled. From reference [1] with permission.

Calculation setup for transport calculations

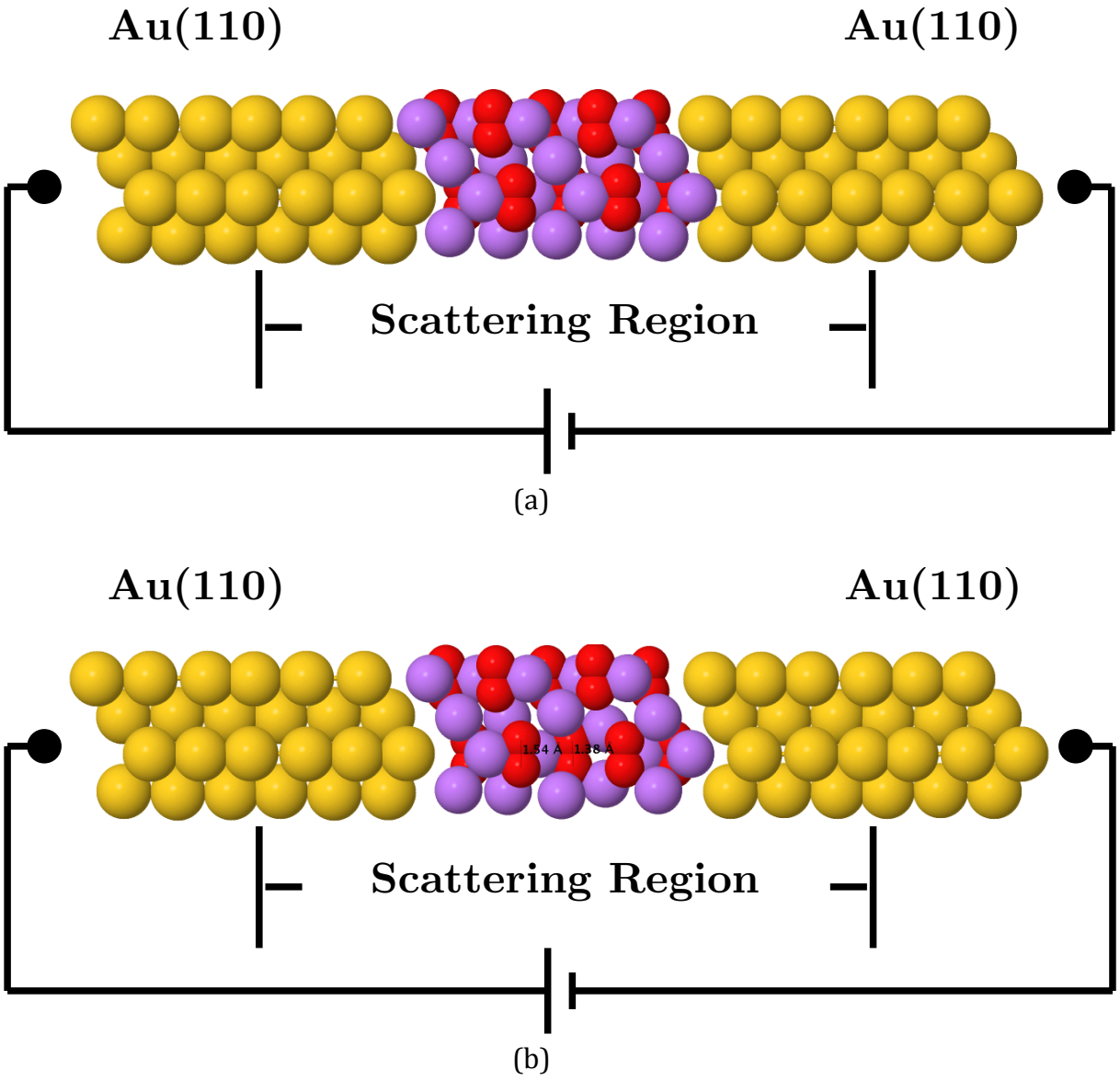

Fig S2. Calculation setup for the MIM charge transport calculations for (a) Stoichometric Li_2O_2 and (b) Li_2O_2 with a bulk Li vacancy. The O-O bond neighboring the Li vacancy contracts by about ~10% and its bond length is 1.38 Å, marked in the figure.

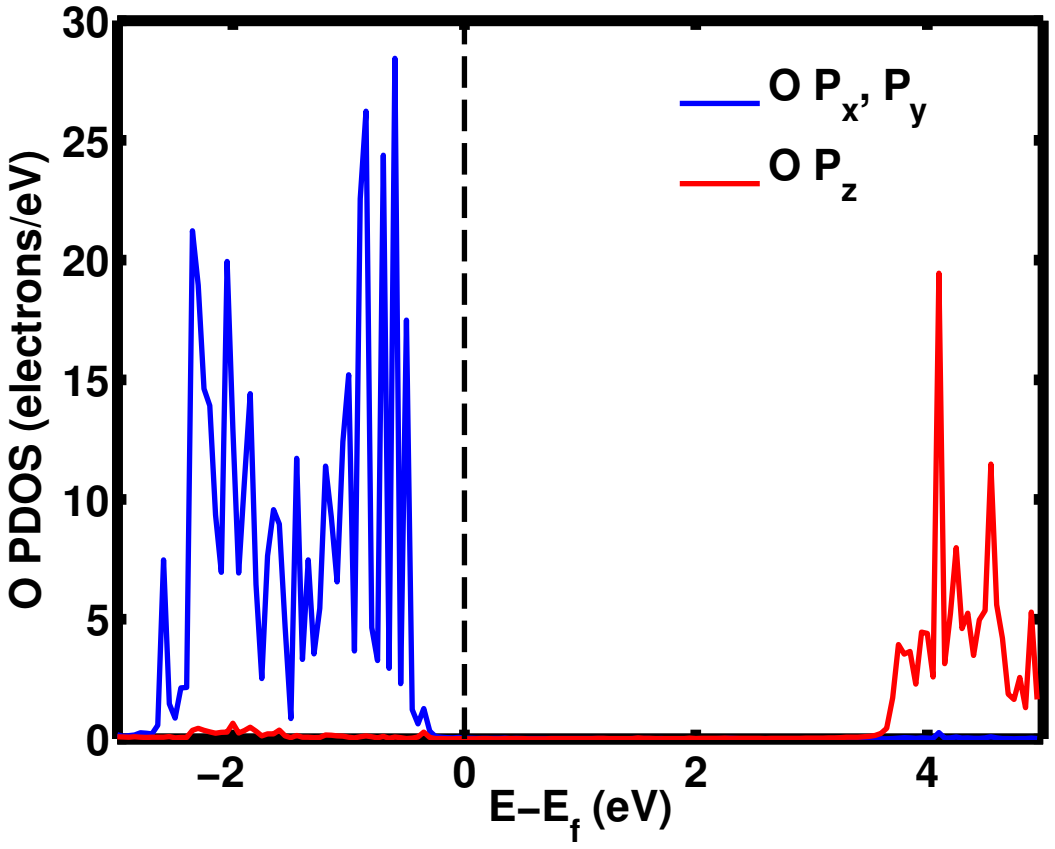

Fig S3: The projected density of states (PDOS) relative to the Fermi Energy for the O atoms of the stoichiometric Li_2O_2 system. As has been shown earlier,[2, 3] the valence band is dominated by O p_x and p_y while the conduction band is dominated by the p_z orbitals. In these MIM calculations, the VBM lies about ~0.4-0.5 eV from the Fermi level.

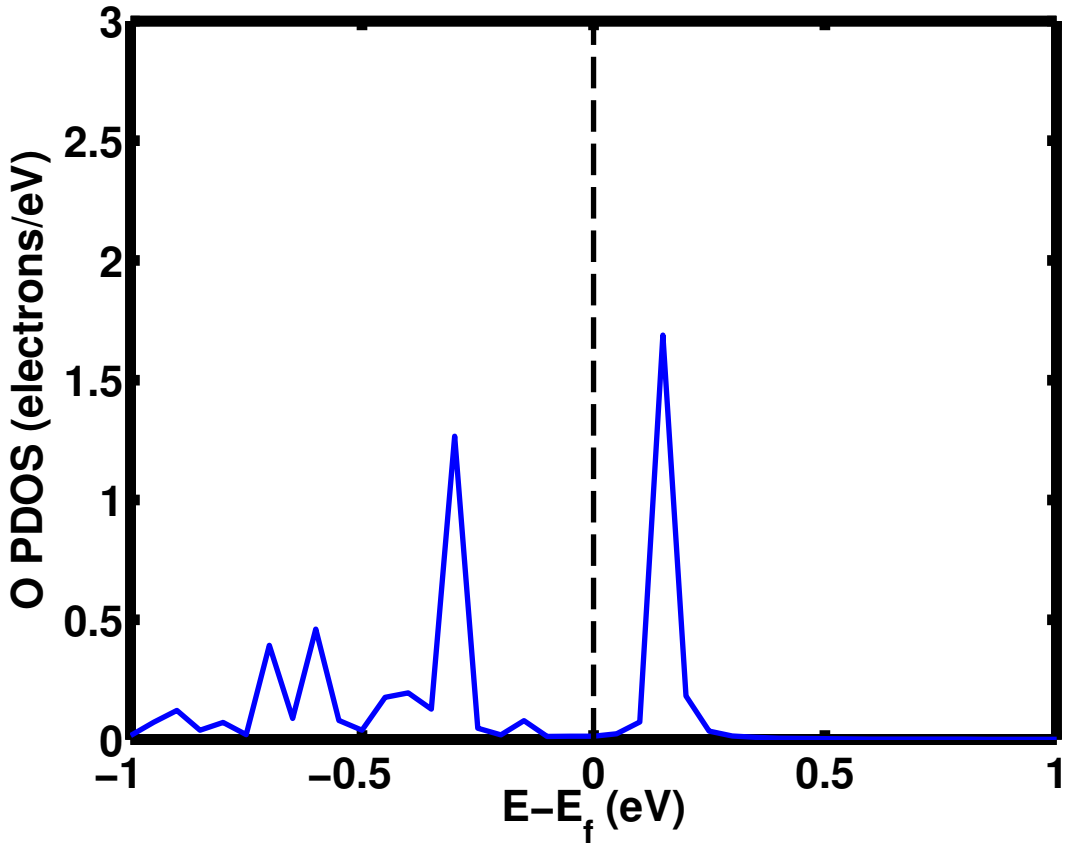

Fig S4: The projected density of states of the O atom closest to the Li vacancy from the charge transport calculations for Li_2O_2 with a bulk defect. There is the emergence of a new unoccupied state just above the Fermi level. As the bias potential is swept, this state becomes occupied and this is shown in Fig 4(b) in the paper.

References:

1. A. C. Luntz, V. Viswanathan, J. Voss, J. B. Varley, J. K. Nørskov, R. Scheffler and A. Speidel, *J. Phys. Chem. Lett.*, 2013, **4**, 3494- 3499.
2. J. S. Hummelshoj, J. Blomqvist, S. Datta, T. Vegge, J. Rossmeisl, K. S. Thygesen, A. C. Luntz, K. W. Jacobsen and J. K. Norskov, *J. Chem. Phys.*, 2010, **132**, 071101.
3. V. Viswanathan, K. S. Thygesen, J. S. Hummelshoj, J. K. Norskov, G. Girishkumar, B. D. McCloskey and A. C. Luntz, *J. Chem. Phys.*, 2011, **135**, 214704.