## SUPPORTING INFORMATION

## Electrochemical Stability of Glyme-based Electrolytes for Li-O<sub>2</sub> Batteries Studied by In Situ Infrared Spectroscopy

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Figure S1: Schematic representation of the cell used to perform in situ FT-IR spectra. 1) Body of the cell, shaped to fit the holder. 2) Pt foil counter electrode. 3) Counter-electrode contact made of Pt wire. 4) Aperture for the reference electrode. 5) Au working electrode. 6) Screw as contact for the Au electrode. 7) CaF<sub>2</sub> prism as the window. 8) and 9) O-rings.

The distance between the gold electrode and the CaF<sub>2</sub> window is adjusted using a micrometric screw attached to 6).



Figure S2: Integrated area between 1141 and 1398 cm<sup>-1</sup>, where the predominant signal corresponds to TFSI<sup>-</sup> vibrations for the potentionstatic SNIFTIRS spectra.



Figure S3: a) Full IR spectra of the remains in the surface of an Au electrode polarized at 4,4 V for two hours, compared to that of the pure salt and solvent used for the electrolyte. The solution tested was 0.1M LiTFSI in TEGDME. b) Zoom in the yellow highlighted low wavenumber region.



Figure S4: SNIFTIRS spectra of LiTFSI-DG 0.1 M during the first cycle in the presence of O<sub>2</sub>.



Figure S5: IR spectra of the remains in the surface of an Au electrode polarized at 4,25V for two hours, compared to that of the pure salt and solvent used for the electrolyte. The solution tested was 0.1M LiTFSI in TEGDME.

An Au electrode was polarized for 2 hours at 4.25V in a LiTFSI in DG solution in presence of oxygen, it was rinsed with water, ethanol and dried. The IR spectrum of the surface of this electrode can be observed in Figure S3, where the presence of glyme peaks can be noticed. Therefore we conclude that the decomposition products of the solvent maintain the -  $CH_3$  and - $CH_2$  groups of the diglyme, and creates a passivating layer on the electrode.