Supplementary Information

## Perfluorinated moiety-grafted carbon nanotube electrode for the non-aqueous lithium-oxygen battery

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## Method

Synthesis of perfluorinated moiety-grafted MWCNT (PFC-MWCNT) via surface modification of MWCNT The surface modification of pristine MWCNTs was carried out in a two-step process (Fig. 1(a)); (i) oxidation of MWCNTs to introduce a higher proportion of carboxylic acid groups (ox-MWCNT) and (ii) esterification of the acid functional groups with a long-chain perfluorinated alcohol (PFC-MWCNT). The procedure described by Byon et al was employed to oxidize the MWCNTs.<sup>1</sup> Briefly, 0.5 g of hand-ground MWCNTs (97% purity, Applied Carbon Nano Technology) were heated with constant agitation for 2 h at 70 °C in 100 ml of a mixed (3:1 v/v) solution of sulfuric acid and nitric acid. The resultant black suspension was then cooled, carefully diluted with 500 ml of 5% hydrochloric acid solution, and filtered over a PTFE filter paper (Millipore Omnipore, pore size 0.45 µm). The filtrate was washed with two further 500 ml aliquots of hydrochloric acid solution, and finally washed with one 500 ml aliquot of deionised water. The resulting black filtrate, i.e. ox-MWCNT (MWCNT-CO<sub>2</sub>H), was then dried at 80 °C overnight and further ground by hand. In the next step, the MWCNT carboxylic acid groups were reacted with a long chain perfluorinated alcohol via a Steglich esterification according to the method described by Martinelli et al.<sup>2</sup> Briefly, 120.5 mg (0.24 mmol) of 1H,1H-nonadecafluoro-1-decanol (98%, Wako Chemical), 49.8 mg (0.24 mmol) of N,N'-dicyclohexylcarbodiimide (99%, Nacalai Tesque), 3.0 mg (0.024 mmol) of 4dimethylaminopyridine (99%, Wako Chemical) and 100.0 mg of ox-MWCNT were placed in a small flask, to which 10 ml dichloromethane was added, then stirred for 24 h. Finally, the product, i.e. PFC-MWCNT (MWCNT-CO<sub>2</sub>CH<sub>2</sub>(CF<sub>2</sub>)<sub>8</sub>CF<sub>3</sub>), was diluted with isopropanol and filtered over a PTFE filter (Millipore FGLP, pore size 0.22 µm), further washed with isopropanol and dried overnight at 80 °C.

**Preparation of PFC-MWCNT and pristine MWCNT electrodes** 20 mg of PFC-MWCNT powder was dispersed in isopropanol by tip sonication for 15 minutes. The suspension was then vacuum filtered through a glass fiber (GF/C, Whatman), the glass fiber then acting as both electrode support and separator for the Li-O<sub>2</sub> cell. After drying at 80 °C, the PFC-MWCNT film on the glass fiber was cut into circular electrodes of 12 mm diameter, with a typical electrode mass of 1.8-2.2 mg. The complete electrode was further dried in a vacuum oven at 80 °C for at least 3 h prior to use. The pristine MWCNT electrodes were prepared by a similar procedure, with careful peeling from the glassy fiber prior to cutting.

 $Li-O_2$  cell assembly and electrochemical measurement The  $Li-O_2$  cells used in this study were custom-designed (Tomcell, Japan). Briefly, the cells consisted of a sealed

negative/positive electrodes assembly, with a self-contained O<sub>2</sub> tank of approximately 40 ml volume. The cells were dried in a vacuum oven at 80 °C for at least 3 h then transferred to an Ar-filled glove box (Kiyon/ALS) with < 5 ppm O<sub>2</sub> and < 1 ppm H<sub>2</sub>O for assembly. The cell was comprised of the following components in ascending order; (i) negative electrode: a stainless steel plate supporting a 12 mm diameter circular film of lithium metal (Honjo), (ii) separator: one piece of Celgard 2500 and one of glass fiber (GF/C), also acting as support for the electrode, (iii) liquid electrolyte: 210  $\mu$ L of 0.5 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 99.7%, Kanto Chemical) in tetraethylene glycol dimethyl ether (tetraglyme, battery grade, UBE) with a water content <10 ppm as measured by Karl-Fischer titration and (iv) positive electrode: either PFC-MWCNT or pristine MWCNT film with a stainless steel mesh current collector (16 mm diameter). After a rest period of at least 8 h under Ar, the cells were purged for 15 min with a constant flow of oxygen (99.9995%, Tomoe Shokai Co. Ltd) of 100 sccm, then sealed.

Galvanostatic discharge/charge was performed using a battery cycler (WBCS3000, WonATech). The applied current (mA.g<sup>-1</sup>) and resulting capacity (mAh.g<sup>-1</sup>) were calculated based on the total electrode mass. Electrochemical impedance (EIS) measurements were performed using a multipotentiostat (VMP3, Bio-Logic) in the frequency range of  $10^{-1}$ – $10^{5}$  Hz at an AC potential of 5 mV. All potentials refer to Li<sup>+</sup>/Li.

**Characterisation** Following discharge/charge, the Li-O<sub>2</sub> cells were purged with Ar for 5 min at 100 sccm then disassembled in the Ar-filled glove box. The positive electrodes were soaked in 2 ml of acetonitrile (<5 ppm H<sub>2</sub>O, 99%, Wako Chemicals) for 30 min, further washed with 2 ml of acetonitrile, and dried overnight under vacuum at 60 °C, with no exposure to ambient air. Thereafter, electrodes were conveyed using hermetically sealed vessels. All characterizations were conducted to observe the electrode surfaces facing the O<sub>2</sub> gas inlet in the Li-O<sub>2</sub> cells.

SEM was performed in a cleanroom with a Hitachi S–4800T and an accelerating voltage of 5-10 kV. TEM images were collected using a JEOL JEM–2100F with an accelerating voltage of 200 kV (field emission). XPS was performed using a VG ESCALAB 250 spectrometer with monochromatic Al K<sub> $\alpha$ </sub> X–ray radiation at 15 kV and 200 W. All spectra were calibrated by setting the C 1s photoemission peak for sp<sup>2</sup>–hybridized carbon to 284.5 eV.<sup>3</sup> FTIR was performed at Thermo Fisher using a Nicolet iS50 spectrometer in transmission mode with KBr pellets. XANES data were collected at BL2 (soft X-ray beamline) for C, O, Li and F K-edges at the synchrotron facility at Ritsumeikan University (SR Center). The following chemicals were used as standards for analysis: Li<sub>2</sub>O<sub>2</sub> (99% purity, Kojundo Chemical Laboratory Ltd, Japan), LiOH (98% purity, Sigma-Aldrich), Li<sub>2</sub>CO<sub>3</sub> (99%, Nacalai Tesque), HCO<sub>2</sub>Li•H<sub>2</sub>O (98%,

Sigma-Aldrich) and LiF (99.9%, Wako Chemical). Sheet resistivity was measured for at least 3 different areas by a four-probe technique using a NPS Sigma-5+ resistivity processor and from which the mean and standard error of mean were calculated.

A home-built online electrochemical mass spectroscopy (OEMS) was employed for chemical and quantitative analysis of evolved gas upon recharge. The apparatus setup was similar to existing reports by McCloskey et al.<sup>4</sup> Briefly, the cell was connected to a 6-way, 2position GC valve (EHLC6WM, Valco). The gas connections to the cell were completed with 1/16" O.D. PEEK tubing for electrical isolation. After a period of gas collection, the contents of the cell were sampled using the GC valve. The sample was then introduced into a crosspiece (high vacuum:  $\sim 1 \times 10^{-3}$  mbar), from which a portion was introduced into the mass spectrometer chamber (ultra-high vacuum ~5 x 10<sup>-8</sup> mbar) via a variable leak valve (951-5106, Agilent). The sampling crosspiece was evacuated with a dry scroll pump (Scroll Meister ISP-250C, Anest Iwata). The mass spectrometer chamber was evacuated with a turbo pump (TurboCube TSU-61, Pfeiffer) system. The gas content of the mass spectrometer chamber was measured with a quadrupole MS residual gas analyser equipped with a Faraday cup detector (RGA 200, Stanford Research Systems). The response of the detector was calibrated with mixtures of gases (typically a series of 5 concentrations in the range 0.00-0.25% vol giving rise to a linear relationship between partial pressure and gas concentration) for O<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub> in Ar. Mass flow controllers (Kofloc) were employed for the accurate preparation of calibration mixtures. The OEMS cell configuration (custom-designed with Tomcell, Japan) is similar to that of the general Li-O<sub>2</sub> cell used for general electrochemical testing except for a considerably smaller headspace volume (2 ml) with inlet/outlet ports for gas with 1/16" valve connectors. The headspace volume of the OEMS cell was measured by comparison with a calibration for volume performed using a series of known volume sample loops (0.25, 0.5, 1, 2 and 5 mL). A detailed description of this process is provided by McCloskey et al.<sup>4</sup>, and is based on the observed pressure rise for each known volume. Quantitative data was thus obtained by consideration of the headspace volume and gas composition. Galvanostatic discharge was performed in a temperature-constant incubator using a single channel potentiostat (Wonatech WPG100e), with an oxygen flow of 10 sccm. During recharge, Ar was used as the diluent and mass spectroscopy measurements were made periodically (typically 15 or 30 min), followed by a short period (1 min) of flushing Ar at 100 sccm through the cell to prevent carry-over of accumulated gas (e.g. O<sub>2</sub> and CO<sub>2</sub>) to the next sample. A LabVIEW program allowed for the automated manipulation of valves and data collection from the pressure gauges and mass spectrometer.



**Figure S1.** TEM images of (a) pristine MWCNT and (b) PFC-MWCNT. The outer layer of PFC-MWCNT is markedly rough compared with that of pristine MWCNT according to chemical surface functionalization.



**Figure S2**. Optical image of 10  $\mu$ l water droplets on the ox-MWCNT (left) and PFC-MWCNT (right) films supported on glass fibers.



**Figure S3.** Galvanostatic cycling discharge-recharge curves of  $\text{Li}-\text{O}_2$  cell with pristine MWCNT electrode in 0.5 M LiTFSI in tetraglyme at a current rate of 70 mA.g<sup>-1</sup><sub>electrode</sub>. The discharge capacity for the 1st and 5th cycle is 1120 and 170 mAh.g<sup>-1</sup><sub>electrode</sub>, respectively.



**Figure S4.** Nyquist plots for as-prepared MWCNT (black squares) and PFC-MWCNT (green circles) cells at an AC potential of 5 mV in the frequency region of  $10^{-1}$ – $10^{5}$  Hz at open circuit potential (OCP). The ohmic resistances (R<sub>s</sub>), associated with solution (electrolyte) resistance with respect to the geometry of the cell, are 13 and 21  $\Omega$  for the MWCNT and PFC-MWCNT cell, respectively, indicated from intersection of the semicircles with the real (Z<sup>2</sup>) axis at high frequency. The intersections with the real axis at low frequency are ~690 and 840  $\Omega$  for MWCNT and PFC-MWCNT cell, respectively. The corresponding fitting plots for as-prepared MWCNT (black dashed line) and PFC-MWCNT (green dashed line) are also depicted on the basis of an equivalent circuit (shown inset), previously reported for a Li-O<sub>2</sub> cell.<sup>5</sup> The fitting results provide the sum of R<sub>ct</sub> and R<sub>interface</sub> as 633  $\Omega$  for MWCNT and 770  $\Omega$  for PFC-MWCNT. Unfortunately, there is an ambiguity in the relative contribution of the R<sub>ct</sub> or R<sub>interface</sub> terms. Moreover, the correspondence between the equivalent circuit and experimental AC impedance measurement is not currently well understood: a number of different equivalent circuit shave been suggested in the literature.<sup>6</sup> Thus the assignment of the resistances in the equivalent circuit (as depicted) is tentative.



Figure S5. SEM image of as-prepared PFC-MWCNT electrode.



**Figure S6.** SEM images of (a) as-prepared and (b) 1st discharged (1DC) pristine MWCNT electrodes. The 1DC MWCNT electrode was conducted with a limited capacity (900 mAh.g<sup>-1</sup> $_{electrode}$ ) that was equivalent to that for the full discharged PFC-MWCNT electrode at a same current rate of 14 mA.g<sup>-1</sup> $_{electrode}$  (see Fig. S7 and Fig. 3(f)).



**Figure S7.** 1DC curves for PFC-MWCNT electrodes in 0.5 M LiTFSI in tetraglyme at current rates of 14, 35 and 70 mA.g<sup>-1</sup><sub>electrode</sub>, corresponding to the SEM images shown in Fig. 3(d–f). The cut-off discharge potential is 2.0 V. The discharge capacity for the 70 mA.g<sup>-1</sup><sub>electrode</sub> (~450 mAh.g<sup>-1</sup><sub>electrode</sub>) is somewhat smaller than the one in Fig. 2(a), which is probably attributed to locally different surface structure and distribution of perfluorinated moiety in the PFC-MWCNT electrodes.



**Figure S8.** OEMS result of 1st recharged (1RC) (a) PFC-MWCNT and (b) pristine MWCNT electrode cells in 0.5 M LiTFSI in tetraglyme at a current rate of 0.1 mA.cm<sup>-2</sup><sub>electrode</sub>. The capacities are normalized to the 1st cycle discharge. Both PFC-MWCNT and MWCNT electrodes demonstrate predominant  $O_2$  gas evolution for the first half RC followed by monotonically increasing  $CO_2$  gas. The increasing  $CO_2$  gas amount is greater for the PFC-MWCNT before the notably decreasing  $O_2$  gas amount. This may be attributed to the existence of oxygen-containing functional groups from the residual free carboxylic acid functionality, which can be less stable and promote the decomposition of the glyme electrolyte.<sup>7</sup>



**Figure S9.** XANES spectra of MWCNT for (a) O and (b) Li K-edge in TEY (black) and partial (for O)/total (for Li) fluorescence yield (grey) modes. 1DC and 1RC are full 1st discharged and recharged MWCNT electrodes, respectively, at a current rate of 0.1 mA.cm<sup>-2</sup><sub>electrode</sub>. References are  $Li_2O_2$ ,  $Li_2CO_3$ , HCO<sub>2</sub>Li, LiTFSI and LiF.



**Figure S10.** XANES spectra of PFC-MWCNT electrodes for (a) F and (b) Li K-edge in TEY (black) and partial (for F)/total (for Li) fluorescence yield (grey) modes. PFC-MWCNT, 1DC and 1RC are as-prepared, 1st discharged and 1st recharged PFC-MWCNT electrodes with the corresponding lithium salts of either 0.5 M LiTFSI or 0.5 M LiClO<sub>4</sub> in tetraglyme. The PFC-MWCNT electrodes were examined with DC to 2.0 V and RC to equivalent capacity, in at a current rate of 14 mA.g<sup>-1</sup><sub>electrode</sub>. References of the LiF, LiTFSI, CF<sub>3</sub>(CF<sub>2</sub>)<sub>8</sub>CH<sub>2</sub>OH precursor (denoted as nonadeca), Li<sub>2</sub>O<sub>2</sub> and Li<sub>2</sub>CO<sub>3</sub> are also depicted.

Residue of TFSI species is observed in the F K-edge spectrum of 1DC-LiTFSI, which can induce a parasitic side reaction to form LiF during discharge. The Li K-edge 1DC-LiTFSI spectra verify the substantial appearance of a LiF-associated peak at 62 eV. Considering the very shallow detection depth of the Li K-edge TEY mode, around 1 nm, the LiF may thinly passivate the topmost surface of Li<sub>2</sub>O<sub>2</sub>. Therefore, it is rational that the LiF can be formed via a reaction between TFSI and superoxide-like species on the topmost surface of Li<sub>2</sub>O<sub>2</sub>. <sup>7,8</sup> To prevent such a parasitic reaction, a non-fluorine lithium salt, e.g. LiClO<sub>4</sub>, can be alternatively employed. As a result, negligible LiF- and fluorine-related species peaks but predominant Li<sub>2</sub>O<sub>2</sub>-related peaks are observed in the Li and F K-edge spectra of 1DC-LiClO<sub>4</sub> in surface-sensitive TEY mode.



**Figure S11.** Galvanostatic discharge-charge curves of PFC-MWCNT for 5 cycles in 0.5 M LiTFSI in tetraglyme at a current rate of 14 mA.g<sup>-1</sup><sub>electrode</sub> under Ar atmosphere. The 1<sup>st</sup> discharge capacity is 12.5 mAh.g<sup>-1</sup><sub>electrode</sub> from OCP to a potential of 2.0 V.

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