Supporting Information

Enhancing the Cycle Stability of Li-O₂ Batteries via Functionalized Carbon Nanotubebased Electrodes

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1) Solubility parameters of materials

In general, the wettability between two materials is determined by how similar the materials are in terms of their respective solubility parameters. The most common way to quantify solubility is by the Hansen solubility parameter (HSP). The HSP, δ , can be calculated using a combination of the solubility parameter information for each examined probe molecule and the adsorption thermodynamic data for each examined probe molecule, as obtained from the inverse gas chromatography (IGC) measurement. The HSP is divided into three different types of partial solubility parameters, dispersion, polar and hydrogen, which are related to the specific intermolecular interaction δ :

 $\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$

Where, d, p, and h refer to the dispersion, polar and hydrogen-bonding interactions. By using the solubility parameter of the substrate and the electrolyte solvent, the solubility parameter distance, R, can be obtained by means of the following expression:

$$R = \sqrt{4(\delta_{gb} - \delta_{gl})^{2} + (\delta_{gb} - \delta_{gl})^{2} + (\delta_{gb} - \delta_{gl})^{2}}$$

The solubility parameter distance provides a quantitative measurement of the degree of similarity between two materials. The solvent with a smaller value of R would form a more stable wettability. Therefore, in order to raise the wettability between electrodes and electrolyte, surface modification should occur in the direction that makes the solubility parameters of the electrodes and the electrolyte similar.

The solubility parameters of all samples are summarized in **Fig. 3a-b**. The dispersion solubility parameters are 19.4, 19.0 and 18.0, for CNT, M-CNT and F-CNT, respectively. The polar solubility parameters are 3.4, 3.45 and 3.5, for CNT, M-CNT and F-CNT, respectively. The hydrogen solubility parameters are 0.2, 0.98 and 1.6, for CNT, M-CNT and F-CNT, respectively. As a result of functionalization, the dispersion parameter decreases and the polar and hydrogen parameters increase.

The solubility distance was obtained by comparing these values to the solubility parameter of EMI⁺TFSI⁻, each having a value of 16.8, 15.5 and 15.4, for CNT, M-CNT and F-CNT, respectively. The better two substances mix, the smaller the value of this R, thus ensuring that the M-CNT and F-CNT sample are better mixed with the electrolyte than the pristine CNT.

2) Active surface area measurement

We investigated how the increased affinity between electrodes and electrolyte affects the performance of the Li-O_2 battery. In general, the electric charge stored in the electric double layer can be calculated through the following equation:

$$C = \frac{\varepsilon_r \varepsilon_0 A}{d} = \frac{\int I dV}{2m\Delta V v}$$

Where ε_r is the electrolyte dielectric constant, ε_0 is the permittivity of a vacuum, A is the electrode specific surface area, d is the effective thickness of the electric double layer (the Debye length), I is the current, V and ΔV are the potential and potential window, m is the mass of electrode material, v is the scan rate and Δt is the discharge time. In this case, all the components except A and $\int IdV$ are fixed and it is known that specific surface area A is proportional to $\int IdV$. Therefore, it is noteworthy that the increasing rectangular area in CV indicates that the area of the electrochemical surface is also increasing.

3) Raman spectrum of CNTs

We analyzed Raman spectroscopy of M-/F-CNT. After the chemical modification, I_D/I_G of CNTs increased from 0.06 to 0.08. On the other hand, the RBM peak, which has the information of the diameter of CNT, remained almost constant even after the chemical modification. Such results indicate that the surface of the DWCNT has been modified as a result of the chemical reaction, whereas the diameter of DWCNT has remained constant.



Fig. S1 Wide and narrow range Raman spectrum of (a, b) pristine CNT, (c, d) M-CNT and (e, f) F-CNT

4) XPS analysis of CNTs

We analyzed C1s & O1s XPS of pristine CNT and M-/F-CNT. After the chemical modification, the ratio of O=C peak in O1s spectrum increased both in M- and F-CNT due to carbonyl bonds in imide group. Also, as shown in **Fig. 2**c, the ratio of C=C of C1s decreased while peaks of functional groups from imide group (imide, C=O, C-N) increased in C1s spectrum of M- and F-CNT. Furthermore, C-F peak appeared in C1s peak of F-CNT, supporting F1s spectrum in **Fig. 2**e.



Fig. S2 XPS spectrum: (a, c, e) C1s of pristine CNT, M-CNT and F-CNT, (b, d, f) O1s of pristine CNT, M-CNT and F-CNT M-CNT and (e, f) F-CNT

5) BET isotherms and pore distribution of CNTs



Fig. S3 BET isotherms and BJH pore distributions of CNTs

	Table S1.	Surface	areas	of CNTs
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	Pristine CNT	M-CNT	F-CNT
BET surface area (m ² g ⁻¹)	258	183	180
BET surface area (m ² g ⁻¹) 50 > d >2 nm	167	155	131

Specific surface areas of CNTs are measured through BET method. According to the measurement, specific surface areas of pristine CNT, M-CNT and F-CNT are 258 m²/g, 183 m²/g and 180 m²/g, respectively. Furthermore, surface area of mesopore of pristine CNT, M-CNT and F-CNT are 167 m²/g, 155 m²/g and 131 m²/g, respectively. Even though the surface area of every pore or mesopore decreases after chemical modification, EASA has increased, indicating surface modification was critical.

6) Partial charge of atoms in functional groups



Fig. S4 Schematic image and partial charge of atoms in (a) maleimide and (b) 3,5-bis(trifluoromethyl)phenyl maleimide

We calculated the charge of N atom in maleimide and 3,5-bis(trifluoromethyl)phenyl maleimide; the charge of N atom was -0.47e and -0.38e, respectively. Since

bis(trifluoromethyl)phenyl group in the molecule is electron withdrawing group, the N atom in F-CNT showed higher oxidation state, resulting in upshift of deconvoluted peaks in N1s spectrum.



7) Partial charge of atoms in functional groups

Fig. S5 Optical microscopy images of contact angle of (a) pristine CNT, (b) M-CNT and (c) F-CNT with EMI⁺TFSI⁻ and Table of Contact angle and work of adhesion of pristine CNT, M-CNT and F-CNT

Contact angle measurements were performed to further determine whether the affinity between the electrodes and the electrolyte was increased by functionalization. As shown in **Fig. S5**, the contact angles of a droplet of electrolyte on pristine CNT, M-CNT, and F-CNT are 40.0°, 35.3° and 31.3°, respectively. This indicates that the functionalized electrodes M-CNT and F-CNT both have better surface wettability by the electrolyte than pristine CNT electrodes. In order to confirm this more quantitatively, the adhesion energy required to separate two adjacent phases was calculated using the Young-Dupre equation. The work of adhesion is about 61.7, 63.8, and 65.1 mJ/m² for pristine CNT, M-CNT, and F-CNT respectively. This means it is more difficult to separate the electrolyte from the functionalized electrodes due an increase in affinity.

7) Elemental composition & FT-IR analysis of CNTs

at(%)	Pristine CNT	M-CNT	F-CNT
Carbon	97.2	95.8	92.1
Oxygen	2.8	3	4.4
Nitrogen		1.2	0.6
Fluorine			2.9

Table S2. Elemental composition of CNTs



Fig. S6 FT-IR spectrum: (a) Transmittance pristine CNT, M-CNT and F-CNT, (b) Transmittance difference of M-/F-CNT to pristine CNT.

We first analyzed CNT electrodes through elemental analysis. According to the results, the amount of nitrogen from imide was about 1.2 and 0.6 at% for M-CNT and F-CNT, respectively. Furthermore, the amount of fluorine was about 2.9 at% for F-CNT. Furthermore, the transmittance difference of the M-/F-CNT to pristine CNT is analyzed. According to the result, we detected the only functional groups of 3,5-bis(trifluoromethyl)phenylmaleimide, which are C-H, C-N and C-F in F-CNT, while we found the only functional group of maleimide, N-H, in M-CNT. Furthermore, we detected C=O in both M- and F-CNT, indicating the functionalization was well done in both CNTs.

8) Temperature dependence of the ionic conductivities



Fig. S7 Temperature dependence of the ionic conductivities of IL/PIL/LiTFSI interlayer film.

The interlayer, an IL-based gel electrolyte consists of pyrrolidinium-based IL and polymeric IL (PIL) matrix with Li salt (LiTFSI), was used to demonstrate a unique 3D folded cell structure with a controlled amount of electrolyte for high energy density in cell level. Due to the viscous behavior of IL and strong interaction with PIL matrix, it showed lower conductivity at room temperature compared to typical liquid electrolytes. As shown in **Fig. S7**,

the interlayer shows the ionic conductivity of 8.6×10^{-5} S/cm at 40 °C, which enables to achieve reasonable resistance at desired thickness. Therefore, it was favorable to test the electrochemical performances of full cells at an elevated temperature of 40 °C. Additionally, the operation in high temperature also enhanced the conductivity of cathode electrolyte, EMI-TFSI, resulting in improved cell performance. Furthermore, to reflect reviews helpful comments, all of above results are added to supporting information.