Supplementary Information for

Principle understanding towards synthetizing Fe/N decorated carbon catalyst with pyridinic-N enriched and agglomeration-free features for lithium-oxygen battery

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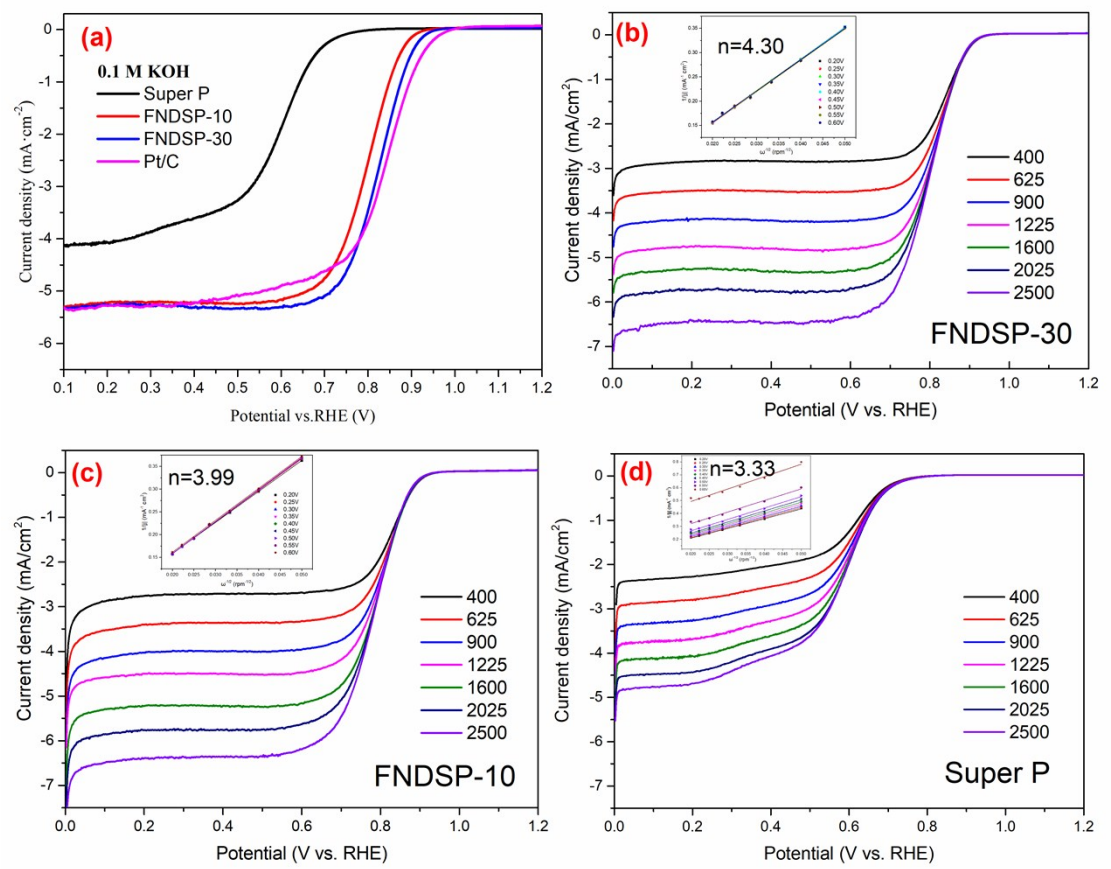

Fig.S1 (a) Linear sweep voltammograms (LSV) curves for ORR of FNDSP-10, FNDSP-30, Super P and commercial Pt/C (20 wt%) at the electrode rotation rate of 1600 rpm and potential scan rate of 10 mV s^{-1}. (b-d) Polarization curves for ORR on FNDSP-30, FNDSP-10 and Super P electrodes in O_2-saturated 0.1 M KOH solution at various rotation rates. The inset images are Koutecky−Levich plots of corresponding materials at different electrode potentials.

The Koutecky-Levich (K–L) plots (J^{-1} vs. $\omega^{-1/2}$) and the electron transfer number (n) and in Fig.S1 (b-d) were obtained using the Koutecky–Levich (K–L) equations below:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_D} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}} \quad (1)$$

$$B = 0.62nFD_{o_2}^{2/3}\nu^{-1/6}C_{O_2} \quad (2)$$

The parameters in above equations are depicted as follows: j, j_k, and j_D are the measured, kinetic, and diffusion limited current densities respectively, ω is the electrode rotating rate, n is the electron transfer number, F is the Faraday constant

(96485 C mol^{-1}), $D_{O_2}$is the oxygen diffusion coefficient ($1.9\times10^{-5}cm^2\ s^{-1}$), ν is the kinetic viscosity of the 0.1M KOH solution (0.01 $cm^2\ s^{-1}$) and $C_{O_2}$is the bulk concentration of oxygen ($1.2\times10^{-3}mol\ L^{-1}$).

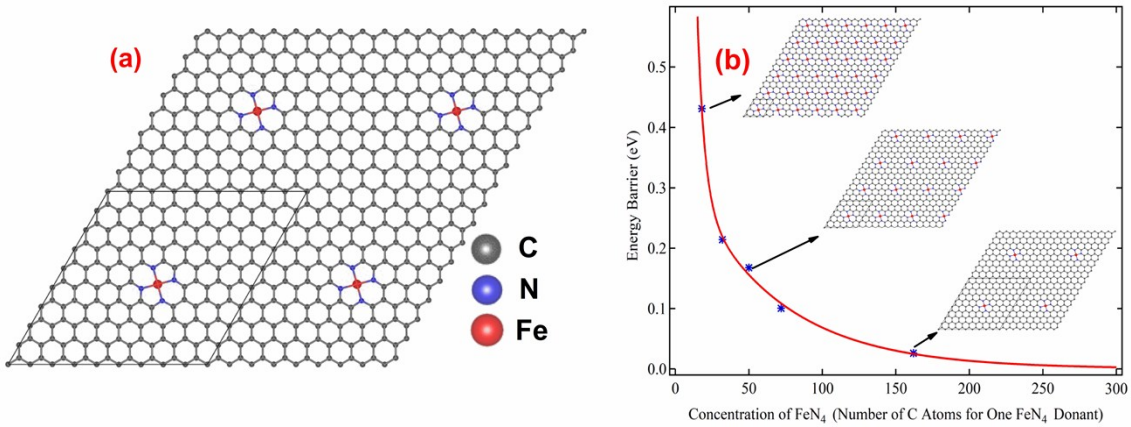

Fig.S2 (a) Atomistic models of FeN_4-doped carbon matrix. Fe, N, C elements are represented in different colors as illustrated. (b) Correlation between rising energy barrier and concentration (number of C atoms for one FeN_4 dopant) of FeN_4 (the blue point is the calculated result by first-principle and the red line is the fitting result).

Table. S1 Comparison of the mean voltages between FNDSP-30 (right side of the slash) and Super P cathode materials (left side of the slash) for Li-O_2 batteries at different cut-off voltages.

Cutoff voltage	Specific capacity（mAh/g）	Mean voltage（V）
2.2V	3963.1 / ---	2.6230 / ---
2.5V	3689.3 / 5811.5	2.6237 / 2.7432
2.6V	2770.7 / 5607.5	2.6355 / 2.7427
2.7V	17.9 / 4706.7	2.7102 / 2.7542
2.8V	--- / 839.7	---/ 2.8156

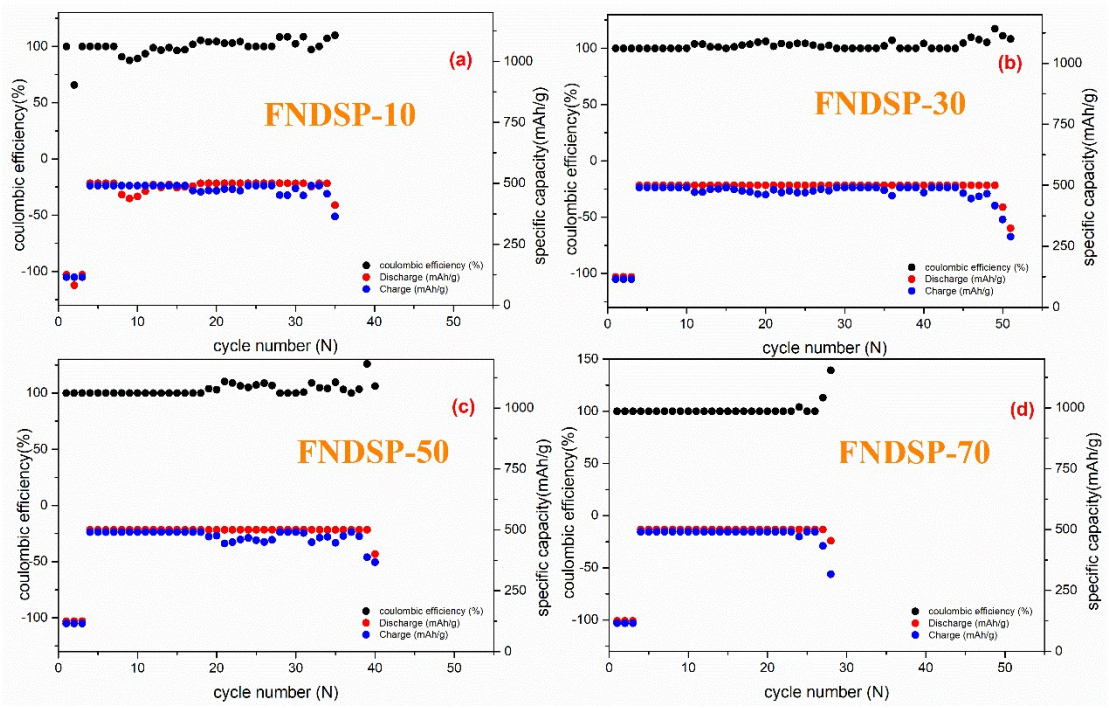

Fig. S3 Discharge capacity and roundtrip efficiency versus the cycle number for Li–O_2 cell with FNDSP air electrode at 0.1 mA.cm^{-2} with the cutoff capacity of 500mAh/g (The initial 3 cycles of Li–O_2 cells used a small cutoff capacity (125mAh/g) to activate the battery).

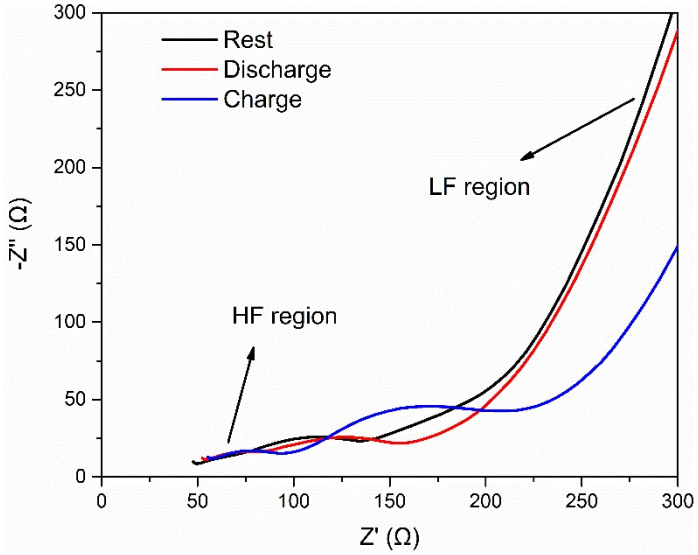

Fig. S4 The a.c. impedance spectra comparison of the Li–O_2 cell using FNDSP-30 electrode before discharge (Rest), after discharge and after charge. The frequency sweep range was 0.1Hz-1MHz with an amplitude of 5mV.

The a.c. impedance spectra were collected on Autolab PGSTAT302N. And we used the FNDSP-30 cathode material as a representation to reflect the impedance variety rules for Li–O_2 batteries at the three states depicted in Fig.S4. The high-frequency semicircle was attributed to the impedance associated with ion adsorption and desorption at the electrified interface, and the impedance decreased according to "after charge" > "after discharge" > "Rest". This result has indicated an increase of the impedance at the electric double layer of the electrode with the raise of discharge-charge depth of the battery.