Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Using Lithium Chloride as a Media to Prepare N, P Co-Doped carbon nanosheets for Oxygen Reduction and Evolution Reactions

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1. Experimental section

Sample preparation: Under the condition of continuous ultrasonic blending, different contents of Lithium Chloride (150mg, 250mg, 350mg) were added into 2 ml phytic acid (50wt%) to form a homogeneous solution. Under Ar atmosphere, the solution was annealed at different temperatures (750 ^{o}C, 800 ^{o}C, 850 ^{o}C) for 2 h. The sample was ground and transferred to a round-bottomed flask with HCl (2 M, 200 mL) to get rid of metal. After sonicated for 20 min, the solution was refluxed for 24 h at 95 ^{o}C. Finally, the sample was filtered and vacuum-dried at 50 °C for 2 h. The sample were annealed at 800 ^{o}C for 1 h In an atmosphere of argon and ammonia at a flow rate of 500ml/min and cooled to room temperature under Ar atmosphere. In the end, the catalysts NPC-“Li” were obtained. The reference NPC was synthesized by using the same procedure without LiCl.

2. Physical characterization

XRD was performed on Cu-Ka radiation (D/Max2000). SEM (FEI/Philips XL30 ESEM) and TEM (FEI/Philips XL30) were conducted to investigate the nanostructure of the prepared catalysts. XPS was measured on Escalab instrument.

3. Electrochemical characterization

All the electrochemical tests were conducted in a typical three-electrode setup with Pt wire, Ag/AgCl and glassy carbon electrode (GCE) as counter electrode, reference electrode and working electrode, respectively. Typically, 3 mg of the prepared catalysts were dispersered into a Nafion solution (60 mL 5 wt% Nafion diluted with 0.35 mL ethanol and 0.15 mL deionized water) and sonicated to form homogeneous ink. 5 μL of the obtained ink was droped onto the GCE and dried naturally. High purity O_2 was used during electrochemical measurement for both ORR and OER. Linear sweep voltammetry (LSV) was obtained with a scanning rate of 5 mV s^{-1}. For zinc-air battery, PTFE and activated carbon with a weight ration of 3:7 was coated onto a nickel foam to prepare air cathode. Then, 230 μL of the ink was dropped onto the air cathode and dried in vacuum oven. Zinc plate and 6 M KOH contained 0.2 M $Zn(OAc)_2$ $2H_2O$ were used as the anode and electrolyte, respectively.

4. Calculation of electron transfer number (n) and % HO_2^- for oxygen reduction reaction

On the basis of rotating disk electrode (RDE) measurements, the electron transfer numbers (n) per O_2 involved in ORR were calculated from the slopes of the Koutecky-Levich plots according to the following equations:[1]

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

Where j is the measured current density, j_k and j_l are the kinetic and diffusion-limiting current densities, ω is the rotating rate of electrode (rpm). B is determined from the slope of the Koutecky-Levich plots according to the Levich equation.

$$B=0.2nFC_{O_2}D_{O_2}^{2/3}\nu^{-1/6} \qquad (2)$$

Where n is electron transfer number per oxygen molecule, F is Faraday constant (96485 C mol^{-1}), C_{O2} is the bulk concentration of O_2 (7.8×10^{-7} mol cm^{-3}), υ is the kinetic viscosity of electrolyte (0.01 cm^2 S^{-1}). D_{O2} is the diffusion coefficient of O_2 in 1 M KOH (1.8×10^{-5} cm^2 S^{-1}).

Hydrogen peroxide yields and the electron transfer number (n) were calculated by the following equations:[2]

$$\%(HO_2^-)=200\times\frac{\frac{I_r}{N}}{I_d+\frac{I_r}{N}} \qquad (3)$$

$$n=4\times\frac{I_d}{I_d+\frac{I_r}{N}} \qquad (4)$$

Where I_d is disk current, I_r is ring current, the collection efficiency (N) was determined to be 0.40 by using 10 mM $K_3[Fe(CN)_6]$.

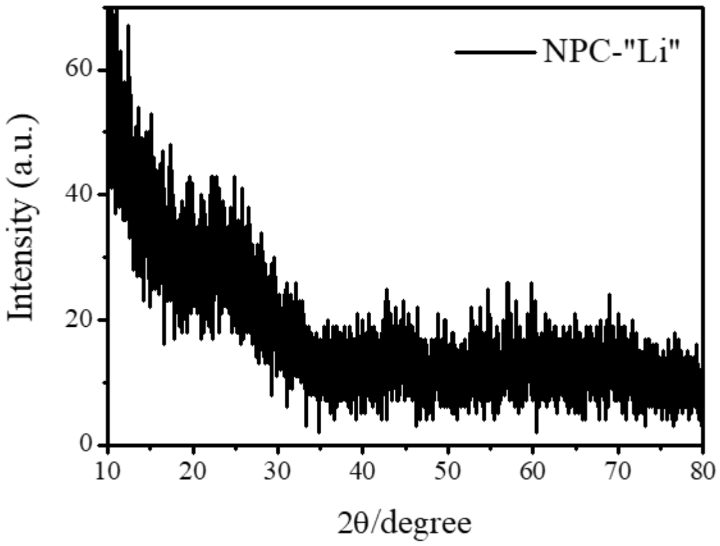

Fig S1. The XRD pattern of NPC-"Li" catalyst.

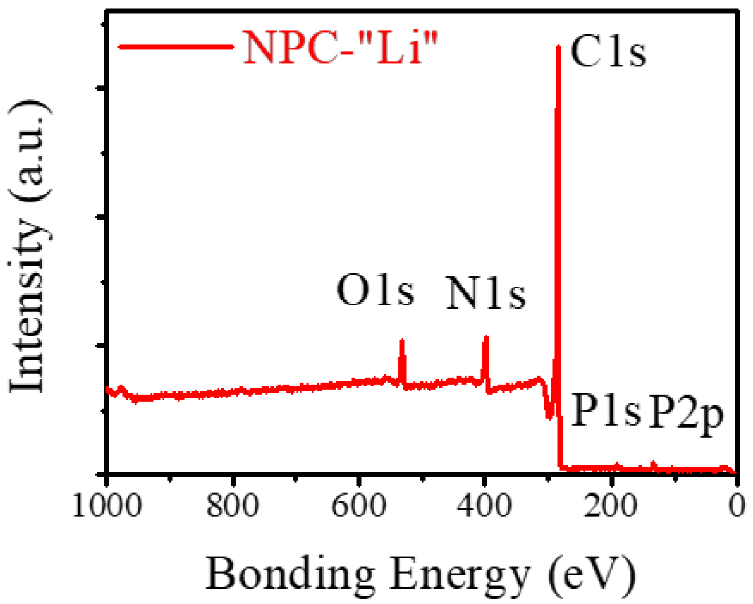

Fig S2. The XPS survey spectrum of the obtained NPC-"Li" catalyst.

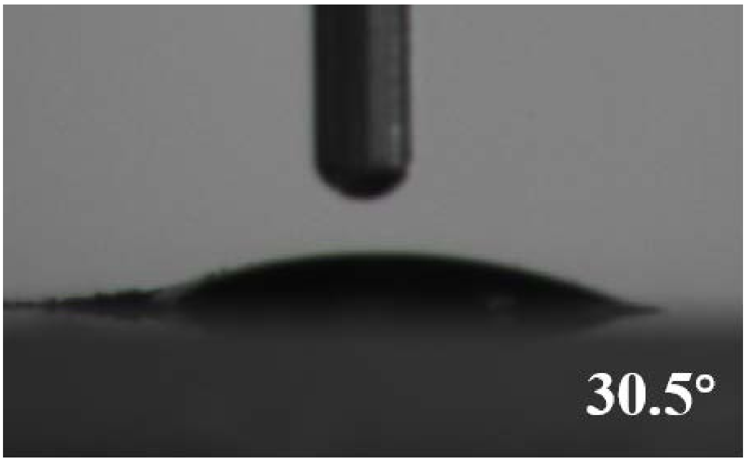

Fig S3. Snapshots for NPC-"Li" catalyst.

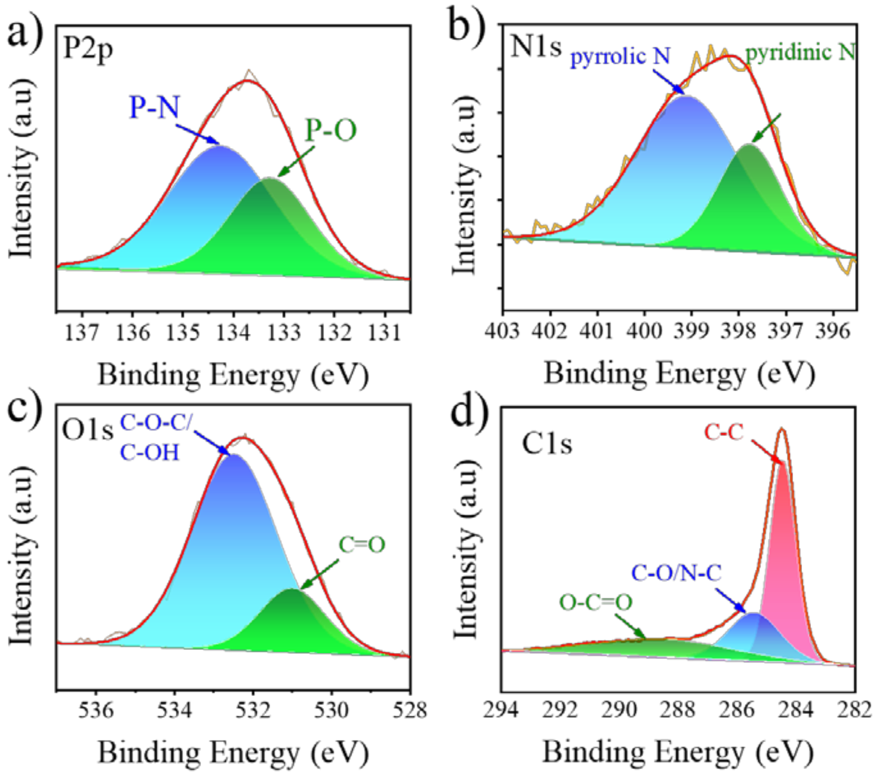

Fig. S4. a) High-resolution of XPS spectra of P2p for NPC. b) High-resolution of XPS spectra of N1s for NPC. c) High-resolution of XPS spectra of O1s for NPC. d) High-resolution of XPS spectra of C1s for NPC.

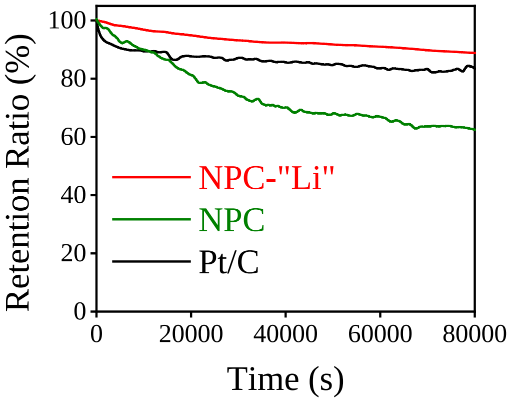

Fig S5. Retention current - time (I - t) curves for NPC-“Li”, NPC and Pt/C at 0.6 V versus RHE.

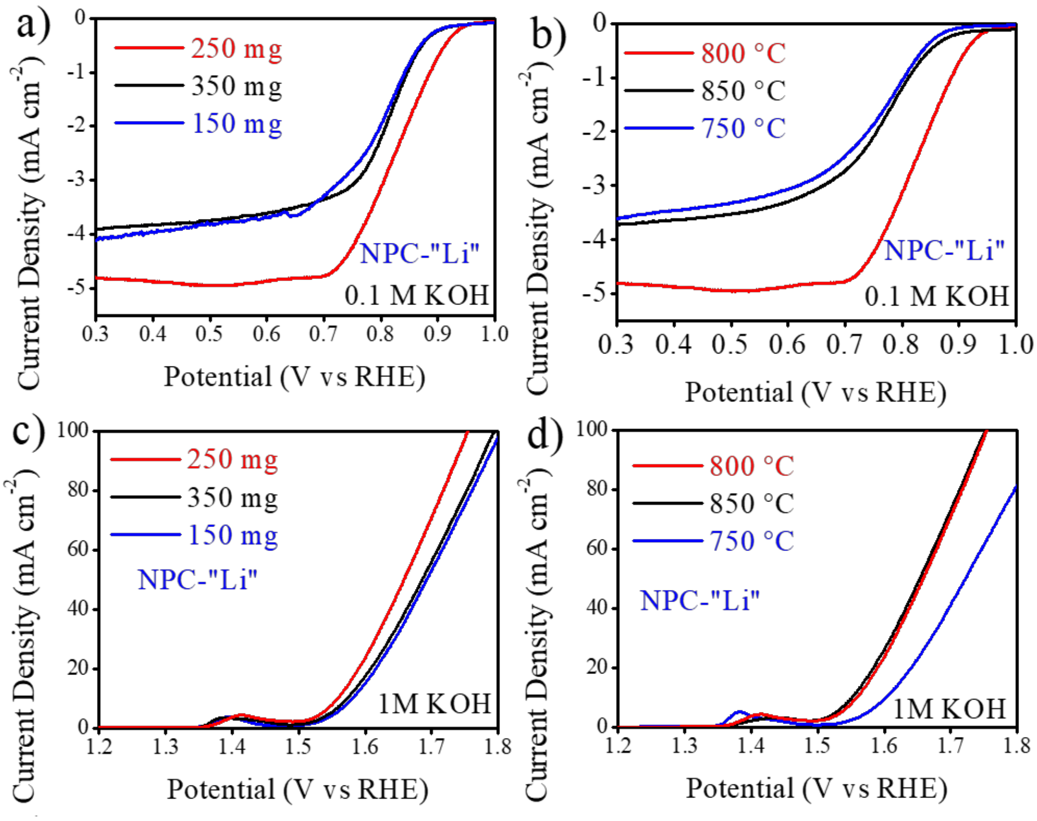

Fig S6. a) LSV of NPC-“Li” for ORR with various content in O_2-saturated 0.1 M KOH. b) LSV of NPC-“Li” for ORR with various temperature in O_2-saturated 0.1 M KOH. c) LSV of NPC-“Li” for OER with various content in O_2-saturated 1 M KOH. d) LSV of NPC-“Li” with various temperature in O_2-saturated 1 M KOH.

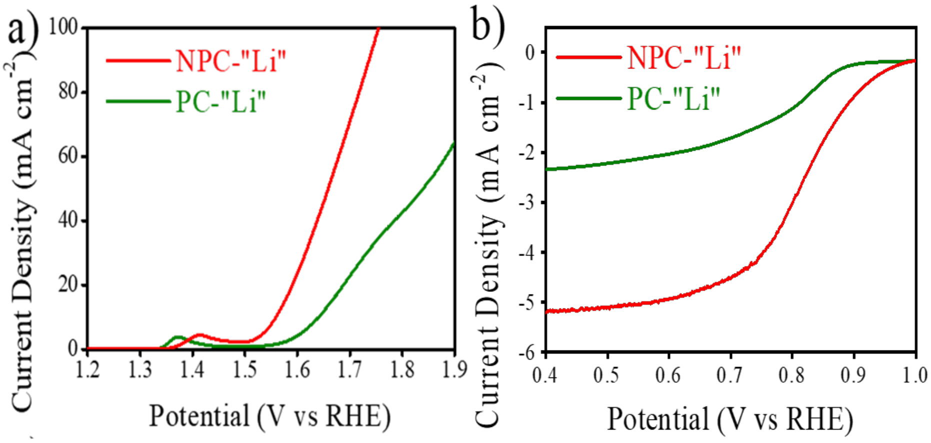

Fig S7. (a) LSVs for ORR of NPC-"Li" and PC-"Li". (b) LSVs for OER of NPC-"Li" and PC-"Li".

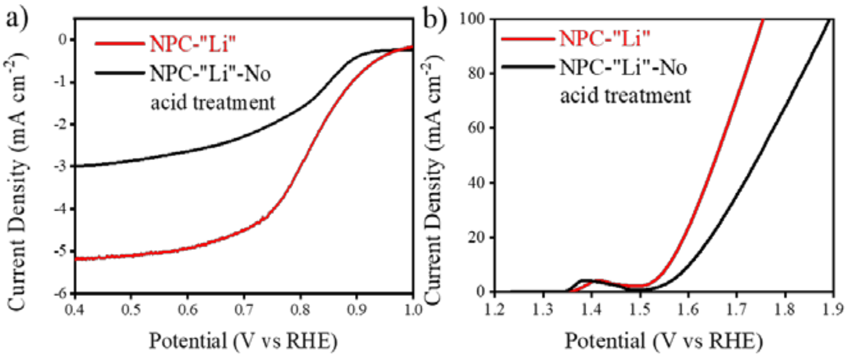

Fig S8. LSVs for ORR of NPC-"Li" and NPC-"Li"-No acid treatment. (b) LSVs for OER of NPC-"Li" and NPC-"Li"-No acid treatment.

Table S1. Comparation ORR performance of NPC-“Li” with reported metal-free catalysts in alkaline electrolyte

Catalysts	Loading (mg cm^{-2})	$E_{1/2}$ (V vs. RHE)	Onset potentials (V vs. RHE)	References
NPC-“Li”	0.21	0.83	1.00	This work
GC-NLS	0.41	0.72	0.85	1
N-doped graphene	0.02	0.79	0.97	2
P-doped ordered	0.16	0.77	0.88	3
Carbon nanotube-	0.49	0.76	0.92	4
N-holey graphitic	0.10	0.78	0.9	5
Fe-PANI/C-Mela	0.51	0.78	0.98	6
NCNF	0.10	0.82	0.97	7
P-g-C_3N_4 grown on	0.20	0.67	0.94	8
P-doped graphite	0.10	0.65	0.82	9
Graphitic C_3N_4/Carbon	0.09	0.67	0.84	10
N,P-CGHNs	0.30	0.82	0.94	11
S-graphene nanoplatelets	0.08	0.62	0.88	12
C_3N_4@carbon	0.28	0.75	0.87	13
B,N-graphene	0.28	0.68	0.86	14
N-graphene quantum dots	0.28	0.65	0.76	15
Porous carbon	0.10	0.79	0.881	16
CNTHb-700	0.30	0.80	0.92	17

Table S2. The performance of rechargeable zinc-air batteries with various electrocatalysts

Catalysts	**Catalyst loading (mg cm^{-2})**	**Specific capacity (mAh g^{-1})**	**Energy density (Wh kgZn^{-1})**	**Cyclability**	**Ref.**
NPC-“Li”	0.70	733@20	908@20	10 min/cycle for 150 cycles; the sum of charge and discharge potentials become smaller	This work
NPMC-1000	0.5	735@5	835@5	10 min/cycle for 180 cycles at 2 mA cm^{-2}; voltage gap increased ~0.7 V	18
NCNF-1000	0.5	660 @5	838 @5	10 min/cycle for 500 cycles ; voltage gap increased ~0.13 V	7
PS-CNFs	1.0	698@5	785@5	12 min/cycle for 600 cycles; negligible change	19
Fe–N/C-700	0.50	703@5	947@5	28h at 25 mA/cm^2 no significant voltage change	20
$La_2O_3/Co_3O_4/$ MnO2–CNTs	2.0	810	970@15	10 min /cycle for 543 cycles； voltage gap increased ~0.10 V	21
FeHis-700	0.5	813@25	960@20	1 h /cycle for 50 cycles; voltage gap increased ~0.15 V	22
Co-doped TiO_2	2.0	785.9@20	911.3@20	20 min / cycle for 3150 cycles, negligible change	23
CNF@Zn/Co NC	0.5	666.7@20	808.2@20	excellent cyclic stability over 150 h， no overt increase of voltage gap	24
FeCo-DHO/ NCNTs	2.00	793.0@20	930.6@20	10min/cycle for 1800 cycles at 5 mA cm^{-2}; no significant voltage change	25
CuS/NiS_2	2.0	775@5	695@25	500 cycles at 25 mA cm^{-2}; the negligible	26

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