Supporting Information

Cobalt and Nickel Phosphates as Multifunctional Air-Cathodes for Rechargeable Hybrid Sodium-air Battery Applications

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Synthesis of NASICON-type $Na_3Zr_2Si_2PO_{12}$:

For the synthesis of NASICON, stoichiometric amounts of $Na_3PO_4 \cdot 12H_2O$, SiO_2 and ZrO_2 were mixed and calcined consecutively at 400 and 1100 °C. After being mixed and calcined again, the powder was pressed into a pellet, which was finally sintered at 1230 °C for 12 h. The NASICON ($Na_3Zr_2Si_2PO_{12}$) pellet was ground with emery paper to have consistent thickness (0.8 mm) and area (2 cm^2, diameter of 8 mm).[R1]

TG-DTA curves:

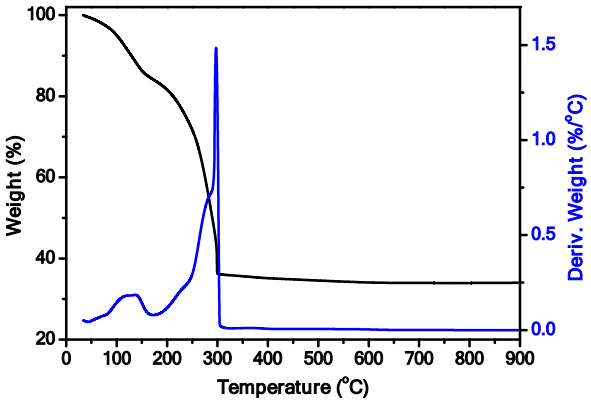


Figure S1. TG-DTA curve of solid precursor $Ni_3(PO_4)_2$.

Raman spectrum:

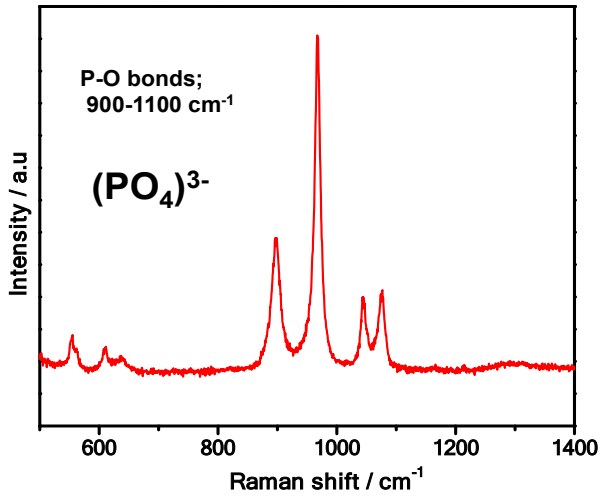
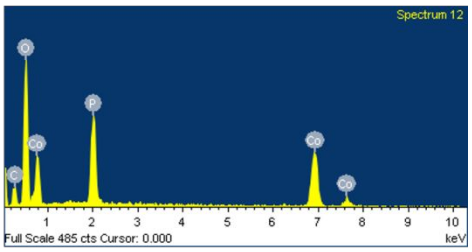


Figure S2. Raman spectrum of $Ni_{1.5}Co_{1.5}(PO_4)_2$ (NCP11) catalyst.

EDS spectra:

CP

Element	Weight%	Atomic%
C K	13.14	23.21
O K	42.98	57.02
P K	12.21	8.36
Co K	31.67	11.41
Totals	100.00	



NP

Element	Weight%	Atomic%
C K	10.27	20.04
O K	36.82	53.91
P K	13.82	10.45
Ni K	39.09	15.60
Totals	100.00	

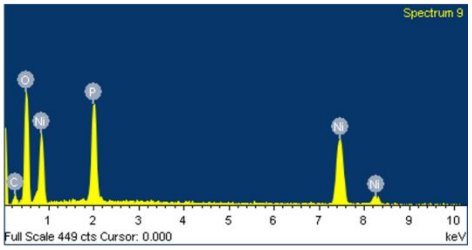
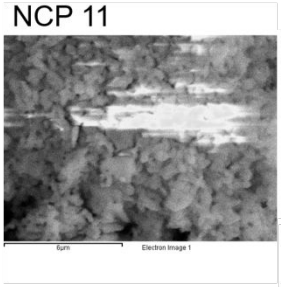


Figure S3. EDX spectra of $Co_3(PO_4)_2$ (CP) and $Ni_3(PO_4)_2$ (NP) samples.

Elemental mapping:

NCP 11



Element	Weight%	Atomic%
C K	8.55	16.29
O K	41.31	59.05
P K	14.76	10.90
Co K	18.28	7.10
Ni K	17.10	6.66
Totals	100.00	

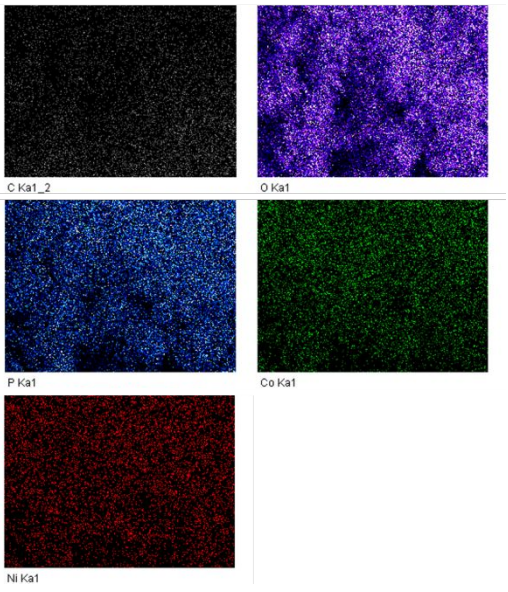


Figure S4. Elemental mapping for the $Ni_{1.5}Co_{1.5}(PO_4)_2$ (NCP11) sample.

XPS Survey spectrum:

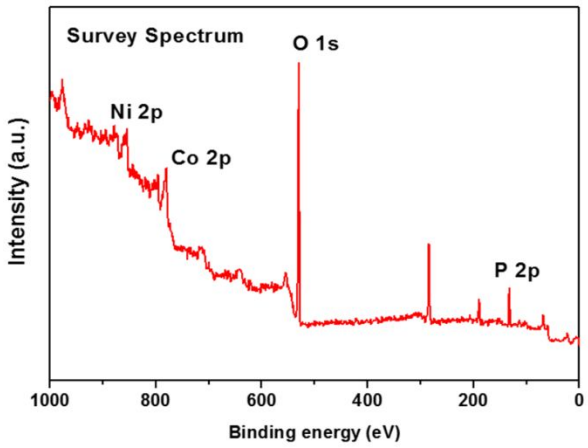


Figure S5. XPS survey spectrum of $Ni_{1.5}Co_{1.5}(PO_4)_2$ (NCP11).

Oxygen evolution reaction studies:

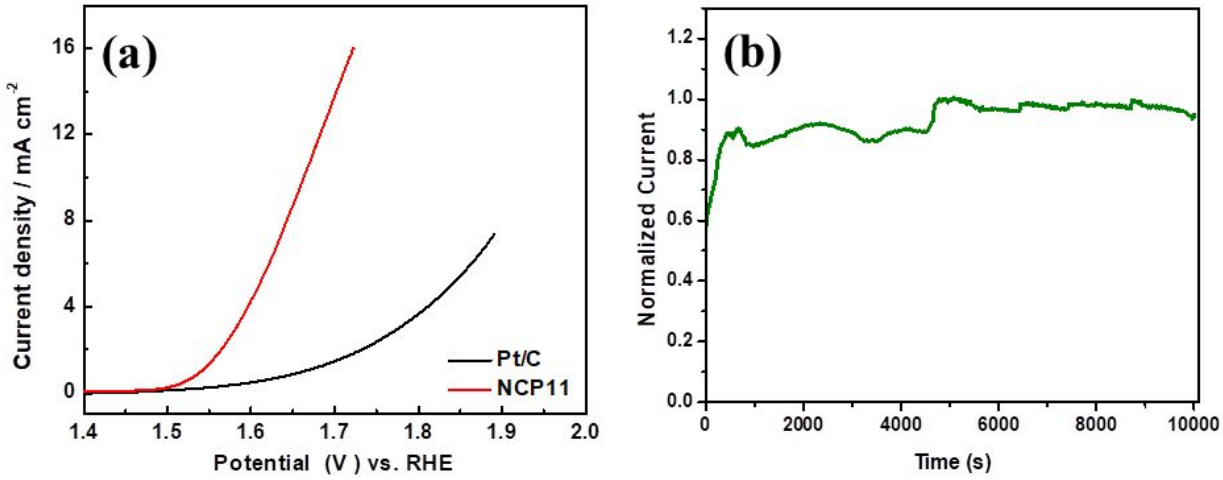


Figure S6. (a) Linear sweep voltammograms of Pt/C and NCP11 at 10 mV s^{-1} in 0.1 M NaOH, and (b) constant potential electrolysis using NCP11 at 1.5 V (vs. RHE).

Calculation of electron transfer number (n) for the ORR:

1. Koutechy–Levich (KL) method

According to Koutechy-Levich theory, the current density behavior on RDE is given by:

$$1/j = 1/j_k + 1/j_L$$

$$= 1/j_k + 1/B\ \omega^{-1/2}$$

where j, j_K and j_L are the measured, kinetic-limited and mass transfer-limited current densities, respectively. The proportionality constant (B) is given by $B = 0.62\ D^{2/3}\ \nu^{-1/6}\ n\ F\ C^*$, where D is the diffusion coefficient of the reactant, ν is the kinematic viscosity of the electrolyte, F is the Faraday constant and C* is the bulk concentration of the reactant. Thus, the electron transfer number (n) can be deduced from the slope of the linear plot of j^{-1} versus $\omega^{-1/2}$ (KL plot).[R2]

2. Rotating Ring Disk Electrode (RRDE) method

In the RRDE method, the ORR is conducted on the disk electrode and H_2O_2 produced is directly measured by oxidizing it on the ring via,

$$HO_2^- + OH^- \longrightarrow O_2 + H_2O + 2\ e^-$$

Then the electron transfer number (n) can be calculated using the equation[R2]

$$n = 4\ i_d / [i_d + i_r / N_c]$$

where i_d is disk current, i_r is ring current (i_r) and N_C is the collection efficiency.

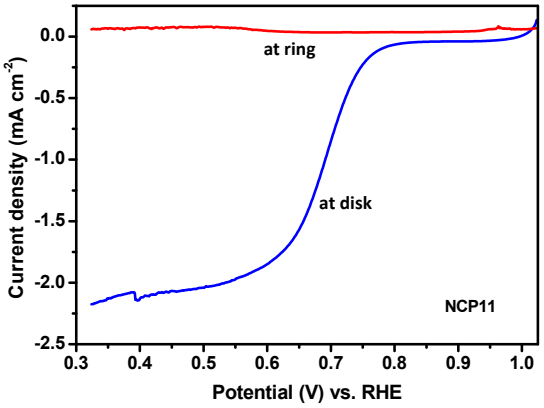


Figure S7. RRDE studies using $Ni_{1.5}Co_{1.5}(PO_4)_2$ (NCP11) catalyst.

Table S1: Structural parameters of combustion synthesized NCP11

Title compound $Co_{1.5}Ni_{1.5}P_2O_8$

Lattice type P
Space group name $P2_1/a$
Space group number 14
Setting number 3

Lattice parameters

a (Å)	b (Å)	c (Å)	alpha (°)	beta (°)	gamma (°)
10.20510	4.71510	5.87200	90.0000	91.0700	90.0000

Unit-cell volume = 282.503 $Å^3$

Structure parameters

			x	y	z	Occ.	B	Site	Sym.
1	Ni	Ni1	0.00000	0.00000	0.50000	0.460	0.800	2d	-1
2	Co	Co1	0.00000	0.00000	0.50000	0.540	0.800	2d	-1
3	Ni	Ni2	0.27500	-0.00300	0.24300	0.295	0.800	4e	1
4	Co	Co2	0.27500	-0.00300	0.24300	0.705	0.800	4e	1
5	P	P1	0.09300	0.42100	0.25500	1.000	0.300	4e	1
6	O	O1	0.10500	0.74600	0.27000	1.000	0.400	4e	1
7	O	O2	0.45900	0.19200	0.25500	1.000	0.400	4e	1
8	O	O3	0.17900	0.31400	0.05500	1.000	0.400	4e	1
9	O	O4	0.16400	0.27100	0.47200	1.000	0.400	4e	1

Table S2: Comparison of OER performance of various catalysts.

Catalyst	Overpotential (V) for 1 mA cm^{-2}	Overpotential (V) for 2 mA cm^{-2}	Overpotential (V) for 4.8 mA cm^{-2}
NCP11	0.233	0.274	0.340
NCP12	0.311	0.335	0.377
NCP21	0.341	0.363	0.405
NP	0.384	0.413	0.467
CP	0.425	0.448	0.493

Table S3: Comparison of round trip efficiency.

Air electrode	Cell design	Round trip efficiency (%)/cycles	Reference
$CaMnO_3$/C	Non-aqueous	55/80	R3
α-MnO_2/rGO	Hybrid	81/20	R4
Pt-graphene	Non-aqueous	68/10	R5
Porous cobalt manganese oxide	Hybrid	74-79/100	R6
VO_2 on rGO-coated carbon paper	Hybrid	81/50	R7
CNT/Ni	Non-aqueous	55/150	R8
Nano porous Au	Hybrid	~80 /18	R9
$Ni_{1.5}Co_{1.5}(PO_4)_2$	Hybrid	1st cycle: 90 ~80 /50	Present work

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