Supporting Information

Sodium Cobalt Metaphosphate as an Efficient Oxygen Evolution Reaction Catalyst in Alkaline Solution

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Experimental section:

Synthesis of NCoM-Cb-Ar and NCoM-Cb-Air: In a typical synthesis, $\text{NaCo}(\text{PO}_3)_3$ was synthesized by solution combustion method using stoichiometric amounts of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (Merck, $\geq 98\%$), $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (Merck, $\geq 99\%$) and $\text{NH}_4\text{H}_2\text{PO}_4$ (SDFCL, $\geq 99\%$) precursors. These precursors were first dissolved in distilled water, then 1 mole of urea (SDFCL, $\geq 99\%$) was added into it. This Na:Co:P mixture was stirred for around 30 min using magnetic bead to get complete homogeneous solution. Resultant reaction mixture was heated at 120°C on a hot-plate with continuous stirring. Finally once excess water evaporated, the temperature was raised to 300°C to propel combustion, which involves exothermic chemical reaction with gaseous evolution to form an intermediate can be named as combustion ash.^{S1} This amorphous intermediate residue was divided into two parts and pelletized. Each pellet was annealed inside a tubular furnace under Ar flow and air atmosphere at 600°C for 6 h to attain the desired final NCoM-Cb-Ar and NCoM-Cb-Air compounds respectively. NFeM-Cb-Ar and NMnM-Cb-Ar were synthesized by replacing $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck, $\geq 98\%$) and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (Aldrich, $\geq 99\%$) respectively.

Synthesis of NCoM-SS-Ar and NCoM-SS-Air: Sodium cobalt metaphosphate $\text{NaCo}(\text{PO}_3)_3$ were also synthesized by conventional solid-state (dry) method by taking stoichiometric amount of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (Merck, $\geq 98\%$), $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (Merck, $\geq 99\%$) and $\text{NH}_4\text{H}_2\text{PO}_4$ (Merck, $\geq 99\%$) precursors. Using (dry) planetary milling all precursors were mixed in Cr-hardened stainless-steel milling media and container for 1 h at 350 rpm. The resulting mixture (raw powder) was again divided into two parts, pelletized, and calcined at 600°C for 6 h under Ar flow as well as air atmosphere to get NCoM-SS-Ar and NCoM-SS-Air respectively.

Instrumentation and characterization techniques:

Material Characterization: Aforementioned as-synthesized samples were primarily characterized by taking powder X-ray diffraction pattern collected at room temperature with a PANalytical X'Pert Pro diffractometer equipped with Cu-K α target of monochromatic wavelength ($\lambda = 1.5418 \text{ \AA}$) operating at 40 kV/30 mA. Diffraction patterns were collected by placing samples on grooved slides with continuous scanning in the 2θ range of 10 - 90° with a scanning step of 0.02626° in Bragg-Brentano geometry. To get lattice parameter and other structural details Rietveld refinement was carried out using GSAS program with the EXPGUI front-end^{S2- S4} for all four samples. A unified picture of the crystal structure of metaphosphate was illustrated using VESTA software.^{S5} Field emission scanning electron microscopy (FE-SEM, FEI Inspect F 50 at 10 kV) was used to compare the size and morphology of the final powder products. Selected area diffraction pattern (SAED) of $\text{NaCo}(\text{PO}_3)_3$ powder was

collected by an FEI Tecnai F 30 STwin TEM (200 kV) microscope. Along with FEI Tecnai F 30 STwin TEM, another electron microscope TEM JNC-JEM-2100PLUS 200 kV electron source (LaB₆) also used to take low resolution TEM images at 120 kV electron source especially for the argon annealed samples to avoid burning of the carbon. Raman spectra of the NaCo(PO₃)₃ samples (as pellet) were recorded on a Horiba Jobin Yvon HR-Raman-123 MicroPL spectrometer with a green laser source of excitation wavelength of 519 nm with a beam spot size of 1 μ m. FT-Infrared absorption spectra of all four powder samples were acquired by PerkinElmer Spectrum100 Series FTIR spectrometer in the wavenumber range of 400-4000 cm^{-1} (cycle number = 4) after diluting the powder with crystalline KBr and pelletizing it into disc. Thermogravimetric (TGA) data was acquired with a TA Q-50 unit. The chemical states of Co in the as synthesized NaCo(PO₃)₃ catalysts powder were analyzed by a Kratos Axis Ultra DLD with an incident monochromated X-ray beam of K α radiation ($h\nu$ = 1486.6 eV) from monochromated Al target. At an accelerating voltage of 13 kV and an emission current of 9 mA, all XPS data were collected. The main carbon signal at a binding energy of 284.6 eV was considered as reference for calibration of shift corrections. These spectra were fitted after Shirley background subtraction using CASA software. Brunauer-Emmett-Teller (BET) surface area of NaCo(PO₃)₃ metaphosphate samples were measured with a Quantachrome Autosorb iQ₂ unit. Prior to the BET analyses, the samples were degassed at 553 K under vacuum for 12 h. Following, the surface area and porosity were measured at 77 K using ultrahigh pure N₂ (99.9995%, Chemix) as the adsorbate.

Electrochemical characterization: The electrocatalytic properties of material were studied using electrochemical work station obtained from CH Instruments (760E, USA). Cells were assembled in three-electrode configuration where catalysts loaded on glassy carbon (GC) (3 mm diameter, 0.071 cm^2) will work as working electrode (WE), coiled Pt as counter electrode and Hg/HgO electrode as the reference electrode. Using this assembly all electrochemical measurements were performed at room temperature using a rotating disk electrode (RDE) in alkaline solution. Before loading the catalyst on the GC-RDE, the electrode was polished with slurry of micro-polish powder (0.05 μ), washed with deionised water and dried. After proper drying the RDE, 5 μ L of catalyst ink (0.14 mg cm^{-2}) was drop casted on the GC surface of RDE and then dried for more than 30 min.

Catalyst ink preparation: For oxygen evolution reaction (OER), 2 mg of each material (NCoM-Cb-Ar, NCoM-Cb-Air, NCoM-SS-Ar, NCoM-SS-Air, NFeM-Cb-Ar and NMnM-Cb-Ar) was dispersed in a mixture of 300 μ L of isopropyl alcohol and 700 μ L of deionised water for 30 min. Finally 5 μ L of nafion was added to this mixture and ultra-sonicated for 30 min.

Experimental techniques for OER activity: All the catalysts were subjected to get polarization data for OER in Ar-saturated 1.0 M KOH (pH ~13.8) which were recorded at a sweep rate of 5 mV s^{-1} with rotation speed of 1600 rpm. Initially in order to activate each catalyst few cycles of cyclic voltammetric (CV) scans (1.20–1.90 V vs. RHE) were used. CV scans in the range of 0.9–1.50 V vs. RHE were also recorded to show the change in redox state and its reversibility at different scan rate. Linear sweeping voltammograms (LSVs) were performed recorded at a sweep rate of 5 mV s^{-1} 1.2 to 1.9 V versus RHE. All measurements were recorded in 1 M KOH after 100 % compensated iR-correction. The EIS data for each catalyst was measured at its onset potential. Thus, EIS for NCoM-Cb-Ar, NCoM-Cb-Air, NCoM-SS-Ar, NCoM-SS-Air, NFeM-Cb-Ar and NMnM-Cb-Ar were recorded at 1.481, 1.521, 1.511, 1.521, 1.591 and 1.551 V respectively vs RHE. All EIS data except NMnM-Cb-Ar were fitted by an equivalent circuit consisting of a solution resistance (R_s), a charge-transfer resistance (R_{ct}), a constant phase element (CPE1) as shown below:

For NMnM-Cb-Ar equivalent circuit consisting of a solution resistance (R_s), a charge-transfer resistance (R_{ct}), a constant phase element (CPE1) and another constant phase element (CPE2) as shown below:

To compare stability of each catalysts accelerated stability tests were also performed at a scan rate of 100 mV s^{-1} for 1000 cycles. Finally, at the end of the LSV cycles, one LSV was recorded for each one to the resulting electrodes at a scan rate of 5 mV s^{-1} . Chronoamperometric (i-t) stability performance of NCoM-Cb-Ar for over 12 h (44000 s) was performed at higher current densities (10 mA cm^{-2}) using GC electrode. The solution was continuously stirred at 800 rpm with constant Ar purging.

Calculation method: Mass activity (MA) has been calculated for three different elements of metaphosphate type NCoM-Cb-Ar, NFeM-Cb-Ar and NMnM-Cb-Ar. The values were calculated from the measured current density J (mA cm^{-2}) at η value of 0.5 V and the catalyst loading which is 0.14 mg cm^{-2} as m , and by using the equation $MA = J/m$ mass activity can be compared. Similarly, specific activity (SA) of the combustion synthesized Co-based catalysts in Ar as well as in air, were calculated from the equation $SA = J/(10 \times m \times S_{BET})$ where, J and m has already been mentioned as current density at $\eta = 0.5 \text{ V}$ and catalyst loading (0.14 mg cm^{-2}). S_{BET} is the BET surface area ($\text{m}^2 \text{ g}^{-1}$).^{S6}

Calibration of Hg/HgO (reference electrode): Hg/HgO (reference electrode) was calibrated w.r.t. reversible hydrogen electrode in 1 M KOH using high surface area coiled Pt electrodes (0.5 mm diameter, 23 cm long) as working and counter electrodes. Prior to the measurements, the solution (1 M KOH) was constantly purged with ultrahigh pure H_2 gas (99.999%, Chemix) for at least 45 min and thereafter a constant flow was maintained during the measurements. Calibration curves were recorded at 1 mV s^{-1} . Thus, the potentials shown in the present work were adjusted according to the following equation: $E_{RHE} = E_{Hg/HgO} + 1 \text{ V}$ (Figure S11).

Table SI. The lattice parameters of $\text{NaCo}(\text{PO}_3)_3$ prepared at different synthetic method and annealing atmosphere.

Catalyst	Lattice parameter ($\text{\AA}$)	Volume ($\text{\AA}^3$)	R_p %	W_{R_p} %
NCoM-Cb-Air	14.2596(02)	2899	5.04	2.81
NCoM-Cb-Ar	14.2534(74)	2895	2.15	3.49

NCoM-SS-Air	14.2785(24)	2911	4.17	2.59
NCoM-SS-Ar	14.2147(90)	2872	3.11	2.16

Table SII. OER activity performance of different catalysts.

Catalysts	Tafel slope (mV dec ⁻¹)	η (V) at J = 10 mA cm ⁻²	S_{BET} (m ² g ⁻¹)	Specific Activity at η = 0.5 V (mA cm ⁻²)	Mass Activity at η = 0.5 V (A g ⁻¹)
RuO ₂	78	0.34	-	-	332
NCoM-Cb-Air	51	0.38	0.61	60	364
NCoM-Cb-Ar	76	0.33	3.70	14	532
NCoM-SS-Air	57	0.39	1.20	27	322
NCoM-SS-Ar	53	0.38	1.60	22	375
NFeM-Cb-Ar	90	0.55	-	-	41
NMnM-Cb-Ar	189	-	-	-	2

Table SIII. Comparison of OER activities of NaCoM-Cb-Ar (as NaCo(PO₃)₃/C) with Co based catalysts from literature.

Materials	Tafel Slope mV/dec	Electrolyte (M, KOH)	Overpotential (mV) at 10 mA/cm ²	Onset Potential (V vs. RHE)	Catalyst Loading mg/cm ²	References
NaCo(PO ₃) ₃ /C	76	1	340	1.54	0.14	Present Work
SrNb _{0.1} Co _{0.7} Fe _{0.2} O _{3-y}	90	0.1	420	1.49	0.23	6
N-CG-CoO	71	1	340	1.55	----	7
ECPT-Co@C	58	1	333	----	0.04	8
G-Co ₃ O ₄	56	1	313	----	0.20	9
G-Co ₃ O ₄	67	0.1	413	----	0.20	9
LiCoO ₂	52	0.1	---	1.55	0.25	10
LiCoPO ₄ /rGO	100	0.1	551	----	0.5	11
Co ₃ (PO ₄) ₂	109	0.1	561	----	0.5	11
Na ₂ CoP ₂ O ₇	51	1	368	1.55	0.40	12
NaCoPO ₄	52	1	389	1.56	0.40	12
NaCo ₄ (PO ₄) ₃	121	Phosphate Buffer	520	----	0.17	13

Figure S1. XRD patterns of NCoM-SS-Ar, NCoM-Cb-Ar, NCoM-SS-Air, and NCoM-Cb-Air samples matching with NaZn(PO₃)₃ phase reported in ICSD in 2θ range of 10-60°.

Figure S2. Pattern indexing of NaCo(PO₃)₃ synthesized by combustion method with final annealing at 600 °C for 6 h in (a) air as well as (b) argon. Similarly NaCo(PO₃)₃ obtained by solid state method annealed in (c) air and (d) argon at 600 °C for 6 h. Pink bars represent the Bragg position for NaCo(PO₃)₃ system.

Figure S3. SEM images of (a) NCoM-Cb-Air, (b) NCoM-Cb-Ar, (c) NCoM-SS-Air, and (d) NCoM-SS-Ar showing the morphology after annealing at 600 °C for 6 h.

Figure S4. TEM images, high resolution (HRTEM) images and the corresponding SAED patterns of (a) NCoM-Cb-Air, (b) NCoM-Cb-Ar, (c) NCoM-SS-Air, and (d) NCoM-SS-Ar catalysts after annealing at 600 °C for 6 h, respectively.

Figure S5. Raman spectra of (a) all four catalyst measured at 514.5 nm; Zoomed version of all four catalysts with no shift as inset. (b) Raman spectra of NCoM-Cb-Ar catalyst recorded at two different regions showing the presence of graphene and phosphate bands together (inset HRTEM of NCoM-Cb-Ar).

Figure S6. FTIR spectra of the Co-based catalysts with various symmetric and asymmetric stretching phenomenon corresponding to PO₂ and POP, vibrational spectra related to PO₄ coordinated units and vibrational bands due to Co/Na-O bonds.

Figure S7. TGA plot of as synthesized NCoM-Cb-Ar catalyst (with rose colour) shows no weight loss.

Figure S8. XPS wide spectra of NCoM-Cb-Air, NCoM-Cb-Ar, NCoM-SS-Air, and NCoM-SS-Ar catalysts from top to bottom.

Figure S9. XPS spectra of C1s in the (a) NCoM-Cb-Air (b) NCoM-Cb-Ar (c) NCoM-SS-Air and (d) NCoM-SS-Ar samples.

Figure S10. Nitrogen adsorption-desorption isotherm curves of (a) NCoM-Cb-Ar and (b) NCoM-Cb-Air catalyst; the corresponding BJH pore size distribution plotted in the inset.

Figure S11. Calibration of the reference electrode (Hg/HgO) in H_2 saturated 1 M KOH solution at 1 mV s^{-1} . Thus, the potentials shown in the present work were adjusted according to the equation: $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 1 \text{ V}$.

Figure S12. OER Linear sweeping voltammograms (LSVs) for combustion synthesized Co, Fe and Mn based metaphosphate catalysts compared with RuO_2 in 1 M KOH Ar-saturated solution at 1600 rpm.

Figure S13. Nyquist plot for NaCoM-Cb-Ar (red), NaFeM-Cb-Ar (pink) and NaMnM-Cb-Ar (purple) during OER at their onset potential and the inset is a zoom of the low impedance region.

Figure S14. Tafel slope plot of various (Co, Fe and Mn) combustion synthesized metaphosphates annealed in Ar atmosphere.

Figure S15. NFeM-Cb-Ar OER LSV recorded at 5 mV s^{-1} (1600 rpm) on the GC rotating disk electrodes before and after 1000 cycles of accelerated stability testing in 1 M KOH.

Figure S16. Cyclic voltammograms of NCoM-Cb-Ar from 0.9 to 1.5 V in Ar-saturated 1 M KOH (a) at different scan rates (50 and 100 mV s^{-1}) and (b) after different cycles (1^{st} and 50^{th} cycles) at 100 mV s^{-1} to show the cycling stability.

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