Supporting Information

$Na_2MnP_2O_7$ Polymorphs as Efficient Bifunctional Catalysts for Oxygen Reduction and Oxygen Evolution Reactions

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Experimental section:

***Synthesis of P*1 NMPy and $P\bar{1}$ NMPy.** Sodium manganese pyrophosphate, $Na_2Mn_2O_7$, was synthesised by mechanochemical assisted solid-state reactions by taking $NaH_2PO_4.H_2O$ (Merck, ≥ 98%) and $Mn(CH_3COOH)_2.4H_2O$ (Merck, ≥ 99%) precursors in stoichiometric ratio. In a typical synthesis, these precursors were dry mixed using planetary ball milling for 3 h at 400 rpm. The resulting precursor mixture was pressed into (green) pellets. These pellets were calcined at 700 ℃ and 555 ℃ for 30 min in Ar atmosphere to get *P*1 NMPy and $P\bar{1}$ NMPy polymorphs respectively.

***Processing of as-synthesised P*1 NMPy and $P\bar{1}$ NMPy.** For electrocatalysis experiments, the as-synthesised active power materials (phase pure products of both polymorphs) were intimately mixed with SuperP carbon black in 2:1 ratio. Mixing was done using ball-milling for 6 h followed by pelletising. These pellets were heat treated at 500 ℃ for 6 h in Ar-atmosphere to form a uniform carbon coating. These calcined pellets were grounded and were used for slurry preparation.

Slurry preparation. To prepare slurry, 2 mg of C-coated NMPy was mixed with 0.75 ml of double distilled water and 0.25 ml of isopropyl alcohol (IPA). This mixture was sonicated for 30 min before adding 2 µl of Nafion as a binder and was further sonicated for 1 h to obtain uniform dispersion. It was repeated for both $P\bar{1}$ and *P*1 NMPy polymorphs. For ORR and OER activity measurement, 5 µl of active slurry was drop-casted onto glassy carbon disk electrode (3 mm dia, part of RDE) and was dried for 30 min under IR lamp with active material loading of ~0.14 mg/cm^2.

Material Characterization:

Physical characterization. As-synthesised polymorphs were probed using powder X-ray diffraction (XRD) with PANalytical X'pert pro diffractometer (Bragg Brentano geometry, Cu K∝ radiation, operating at 40 kV/30mA) in the 2θ range of 10°-90° at scanning step size of 0.02626°s^{-1}. The sample purity and structural parameters were evaluated by Rietveld analysis using FULLPROF program aided with visualization in WinPLOTR.[1,2] Pseudo-Voigt function was used for peak shape approximation and background was fitted using linear interpolation.

The structural details for both $Na_2MnP_2O_7$ pyrophosphate polymorphs are tabulated in Table S1 and S2. The structural illustration was performed using VESTA 3D visualization software.[3] Morphology was observed using field emission scanning electron microscopy (FE-SEM, FEI Inspect F 50 operating at 10 kV). Morphology and structural features were further analysed with an FEI Tecnai F30 STwin transmission electron microscope (operating at 200 kV). High resolution (HR)-TEM images and selected area diffraction patterns (SAED) were acquired. Mn oxidation states was probed by X-ray photoelectron spectroscopy (XPS) where monochromator X-ray beam of Al target was used having Kα radiation (ħν = 1486.6 eV) accelerated at 13 kV and 9 mA. The shift corrections were calibrated by taking carbon signal with binding energy 284.6 eV as reference. All the spectra were studied using CASA software and background was fitted using Shirley background subtraction.[4]

Electrochemical characterization. Oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) study was performed in 0.1 M KOH electrolyte. A CH Instruments (7001E, USA) electrochemical workstation was used to perform electrochemical studies with standard Hg/HgO reference electrode and Pt wire as counter-electrode. The catalyst was drop casted on rotating ring disk (RDE) and was used as working electrode. The cyclic voltammetry (CV), and linear sweep voltammetry (LSV) techniques were conducted at a scan rate of 10 mVs^{-1}. The loss in current density was measured after prolonged LSV (for 500 cycles) for both NMPy polymorphs. Chronoamperometry (ORR Stability) test was performed for over 28,800 s at -0.4 V (vs. Hg/HgO reference electrode) for both polymorphs of $Na_2MnP_2O_7$.

Postmortem Analysis. Using rotating disk electrode (RDE) measurements, change in morphology after ORR and OER has been examined in the potential window of 0.25 to 0.95 V and 1.1 to 1.8 V (vs RHE) region respectively.

Potential Calibration. For the electrochemical measurements, the potentials in the present study were recorded by Hg/HgO as reference electrode and were converted into reversible hydrogen electrode (RHE). Potential calibration of the reference electrode (Hg/HgO) was carried out in 0.1 M solution at 1 mV/s. Thus, the potentials shown in the present work were calculated by the equations:

$$E_{RHE} = E_{Hg/HgO} + 0.897 \text{ V for 0.1 M KOH} \quad \text{(Figure S1)}$$

n calculation during ORR. Experimentally number of electron (n) was calculated from Koutecky–Levich (K-L) theory (equation 1), which was deduced from LSV plots measured at different rotation for different catalysts. Slope obtained from K-L plot can be represented as 1/B from which number of electrons can be calculated. Thus eq 2 was analysed and the number of electron was calculated from RRDE measurements.

$$\frac{1}{j} = \frac{1}{j_K} + \frac{1}{j_L} = \frac{1}{B}\omega^{-1/2} + \frac{1}{j_K} \qquad (1)$$

where, j, j_k, and j_L represents the measured, kinetic-limited, and mass-transfer-limited current densities, respectively. Further, kinetic-limited current density, j_k is assumed to be a constant at a certain potential and mass-transfer-limited current density, j_L is proportional to the $\omega^{1/2}$ (ω = angular velocity) of the RRDE. The proportionality coefficient B can be expressed as,

$$B = 0.62D^{2/3}v^{-1/6}nFC^{*} \qquad (2)$$

where D is the diffusion coefficient of O_2 (1.9×10^{-5} cm^2 s^{-1} for 0.1 M KOH), v is the kinetic viscosity of the electrolyte (0.01 cm^2 s^{-1} for 0.1 M KOH), n is the number of electron, F is the Faraday constant, C^* is the bulk concentration of O_2 (having value of 1.2×10^{-6} mol cm^{-3} in 0.1 M KOH).

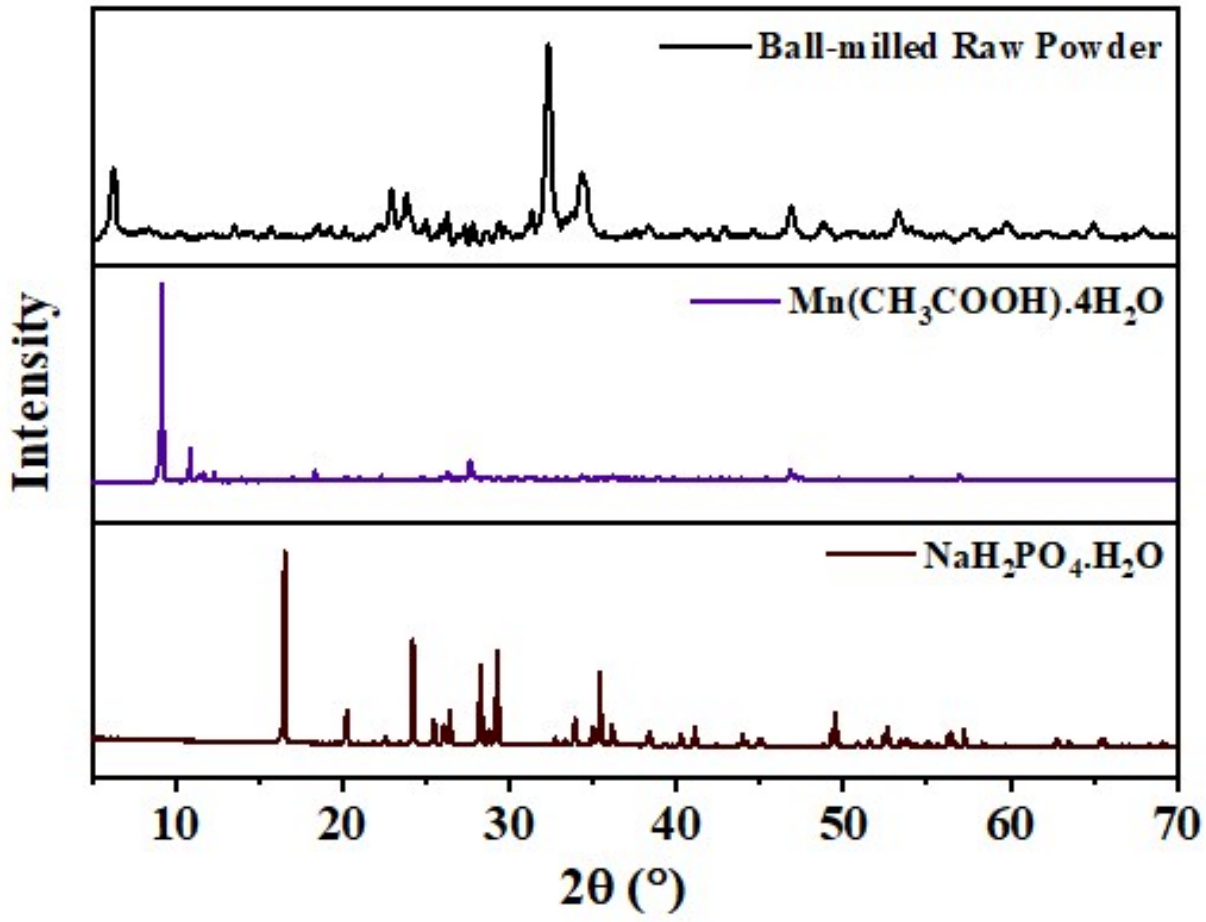

Figure S1. XRD patterns of both precursors and intermediate powder recovered after planetary ball milling which is subjected to different temperatures to obtain $Na_2MnP_2O_7$.

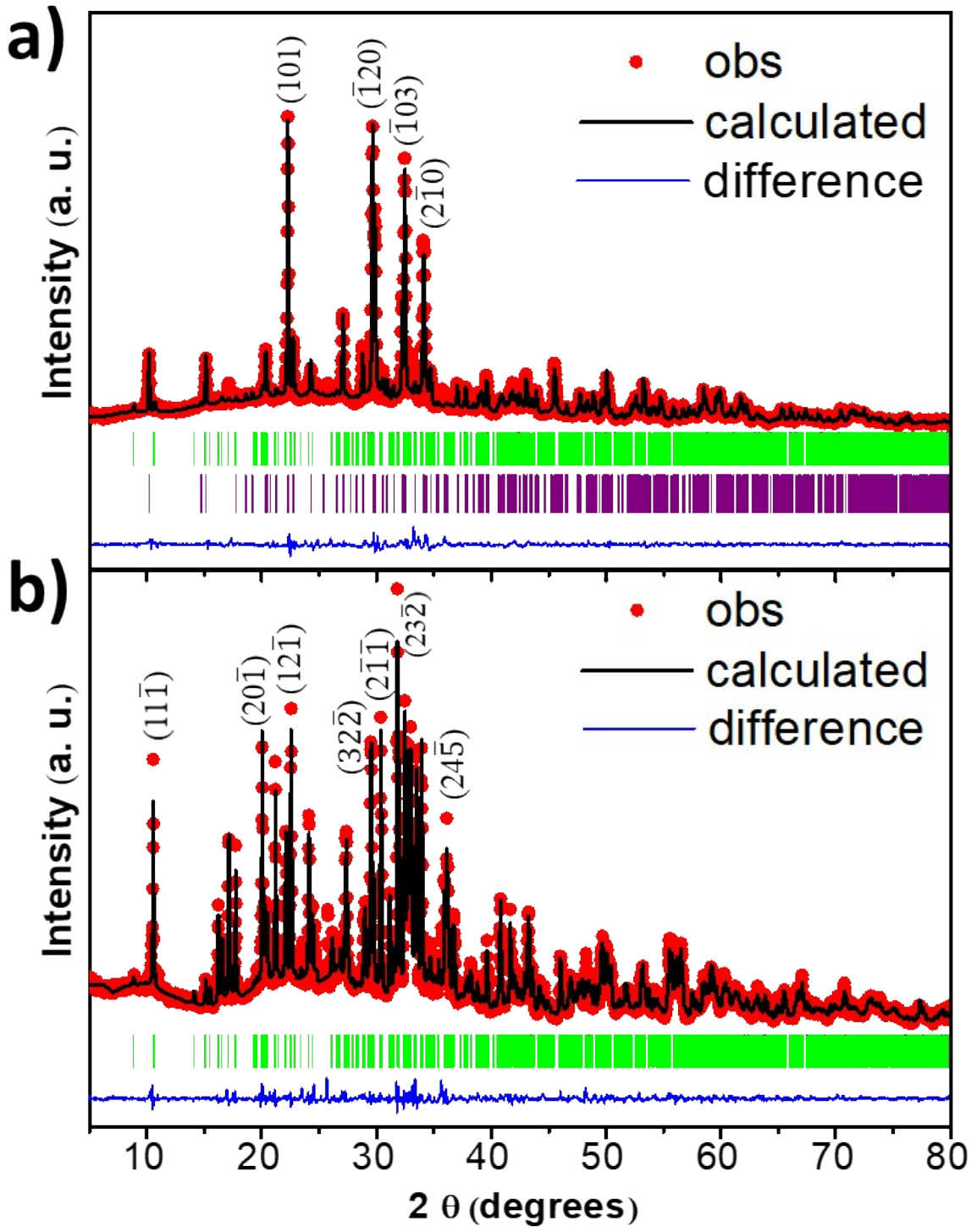

Figure S2. Rietveld refined XRD patterns of both polymorphs of $Na_2MnP_2O_7$ (a) $P\bar{1}$ NMPy and (b) $P1$ NMPy, with (hkl planes) of their major XRD peaks. The observed (Iobs) and calculated (Ical) intensities are represented by the red dots and black solid lines respectively. The bottom blue line shows Iobs-Ical with Bragg positions for each phase as green vertical ticks with little impurity of another polymorph.

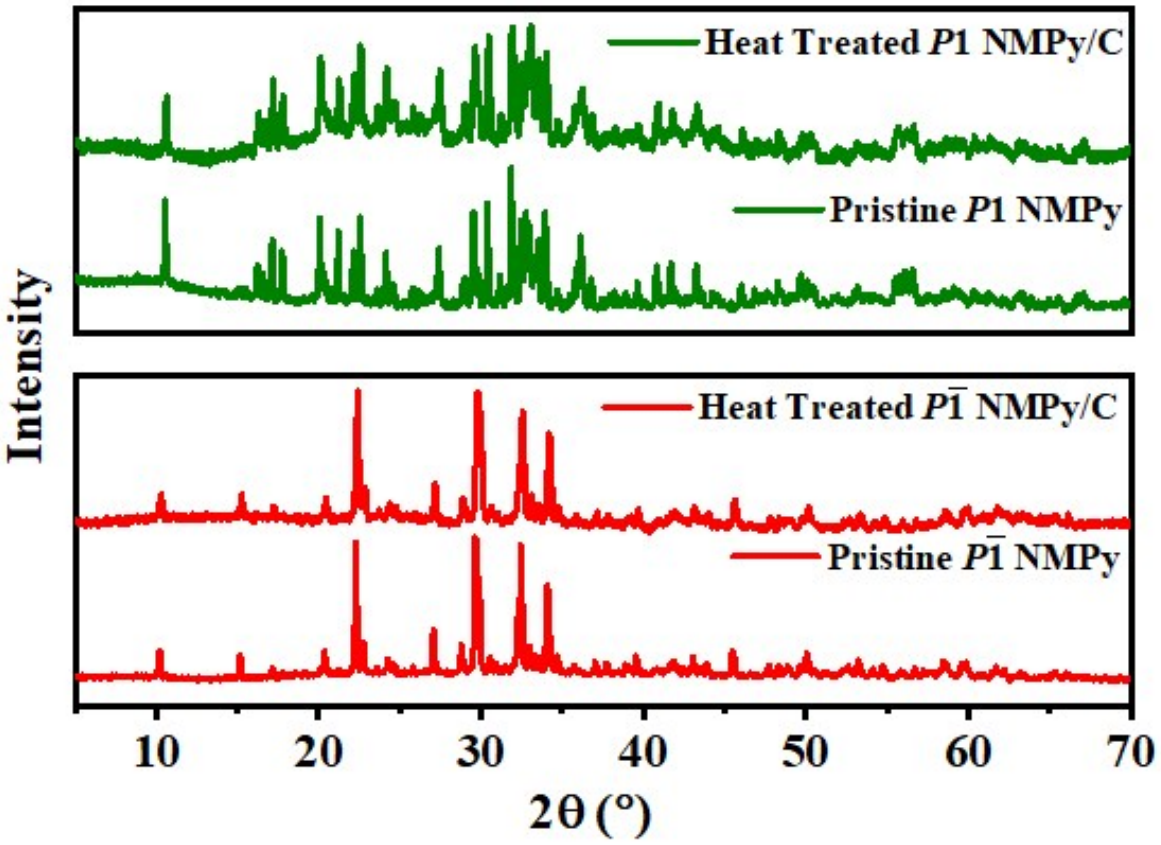

Figure S3. XRD pattern of as-synthesized polymorphs of $Na_2MnP_2O_7$ named as pristine and heat-treated $Na_2MnP_2O_7$ powders mixed with SuperP carbon used for electrocatalysis (mentioned in "processing of as-synthesised *P*1 NMPy and $P\bar{1}$ NMPy" section).

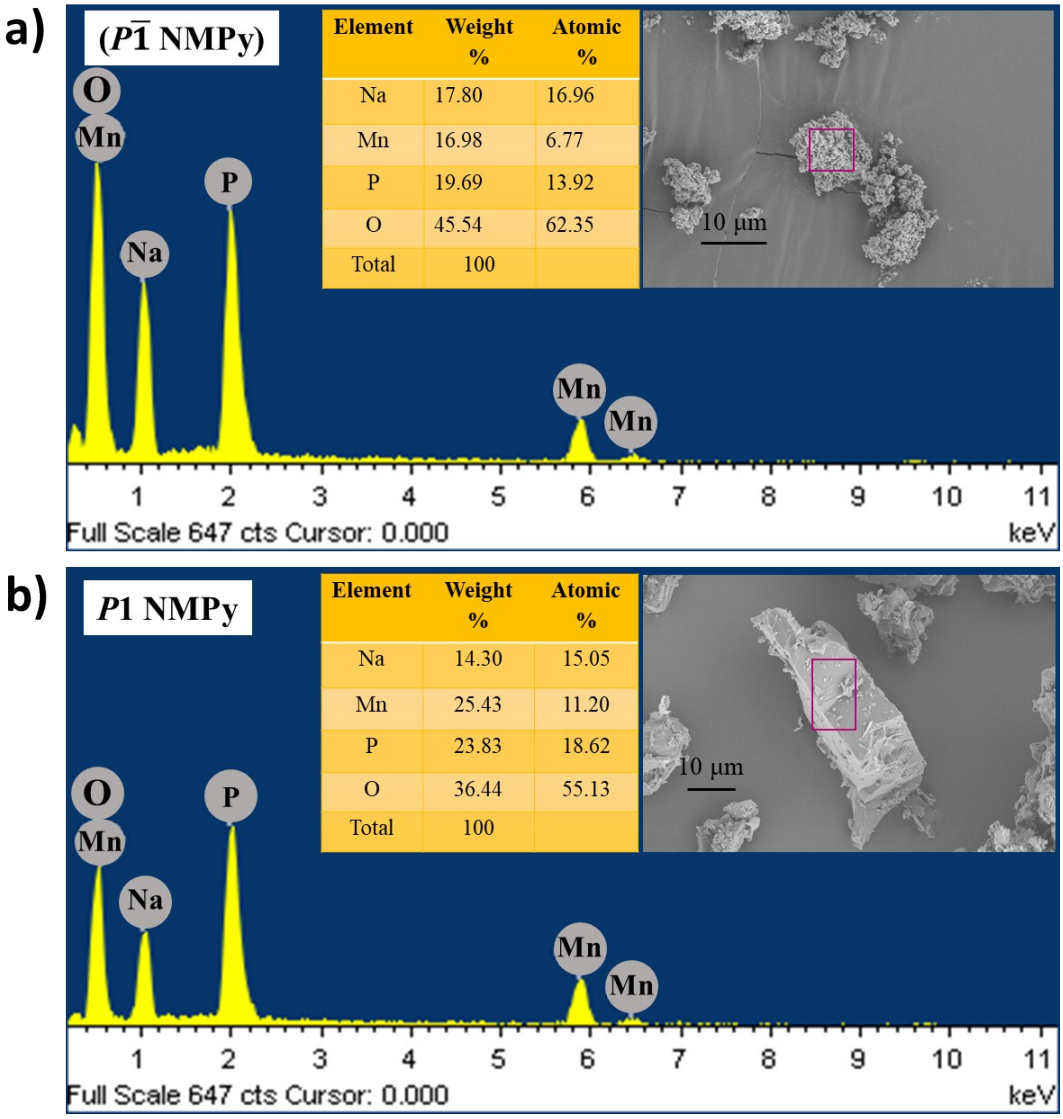

Figure S4. Scanning electron microscopy (SEM) images of as-synthesized polymorphs of $Na_2MnP_2O_7$, (a) $P\bar{1}$ NMPy and (b) $P1$ NMPy along with energy disperse X-ray spectrometry (EDS) of the elemental weight percent (Weight %) and atoms percent (Atomic %) at an area shown with pink rectangle over sample.

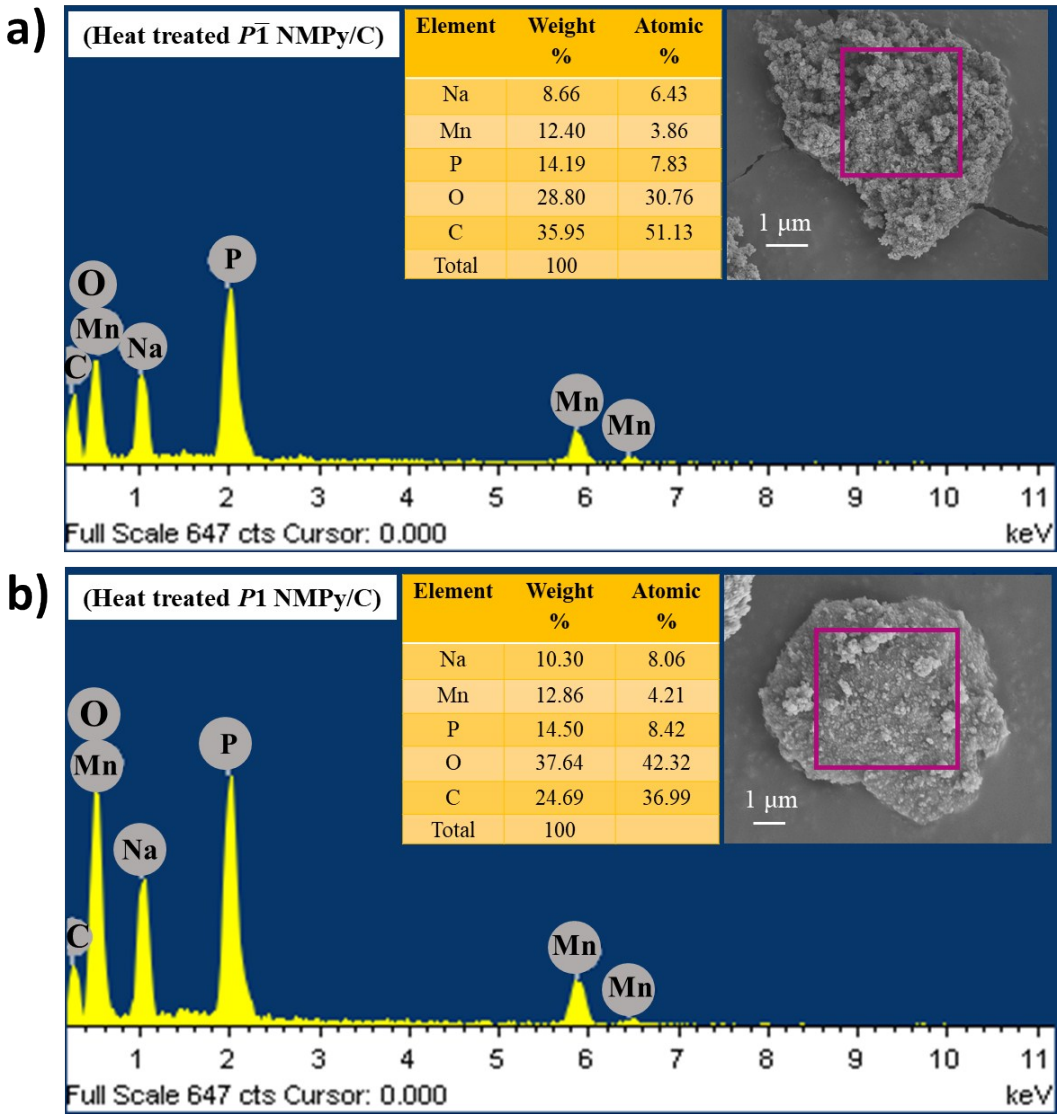

Figure S5. Scanning electron microscopy (SEM) images of heat treated polymorphs of $Na_2MnP_2O_7$, (a) $P\bar{1}$ NMPy/C and (b) $P1$ NMPy/C along with energy disperse X-ray spectrometry (EDS) of the elemental weight percent (Weight %) and atoms percent (Atomic %) at an area shown with pink rectangle over sample.

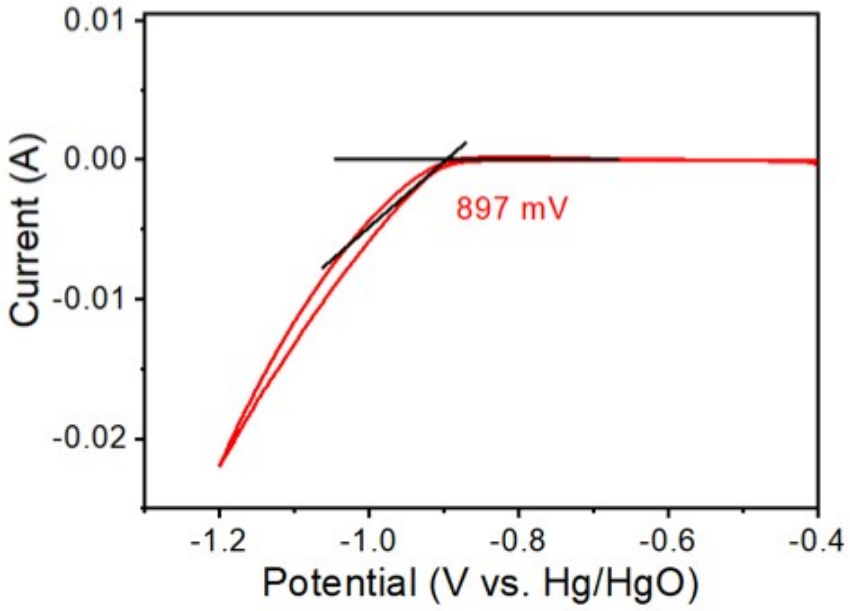

Figure S6. Potential calibration of the reference electrode (Hg/HgO) in 0.1 M KOH solution at 1 mV/s. Here, the potentials were calculated by the equation: $E_{RHE} = E_{Hg/HgO} + 0.897$ V.

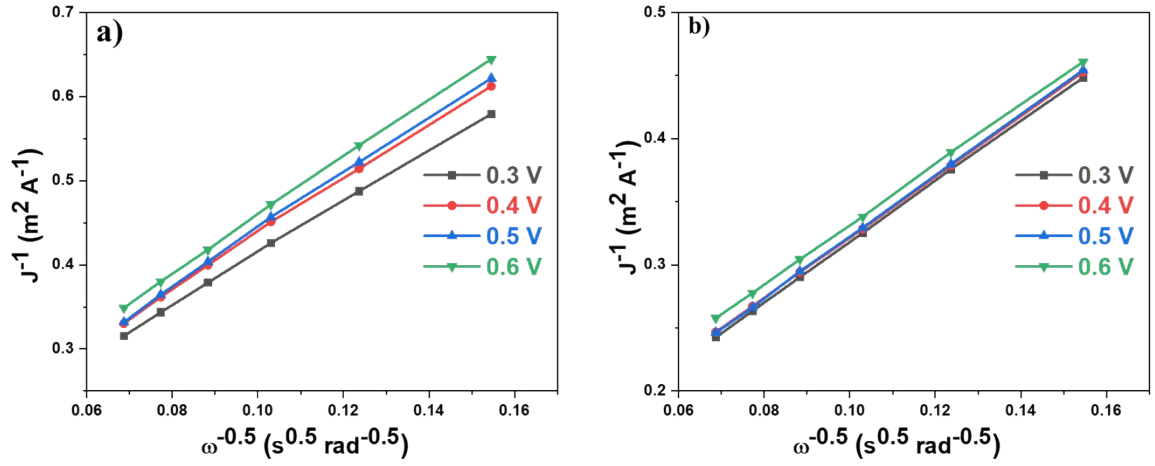

Figure S7. Koutecky-Levich plots (J^{-1} *vs* $\omega^{-1/2}$, J is the current density in A m^{-2} and ω is the rotating speed in rad s^{-1}) of both polymorphs of $Na_2MnP_2O_7$: (a) NMPy-$P\bar{1}$, and (b) NMPy-*P*1.

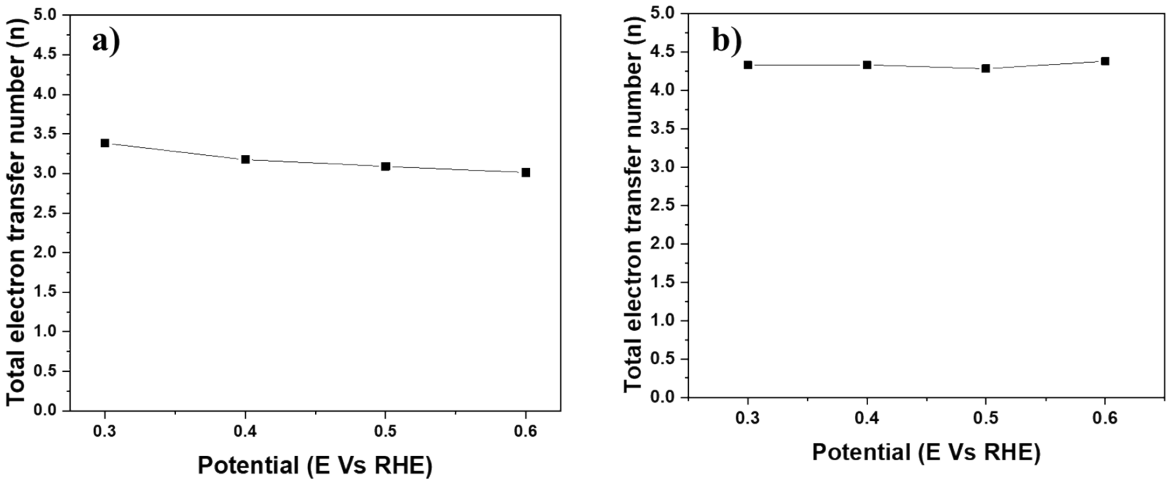

Figure S8. Number of electrons transfer during ORR for both polymorphs of $Na_2MnP_2O_7$ (a) NMPy-$P\bar{1}$, and (b) NMPy-$P1$.

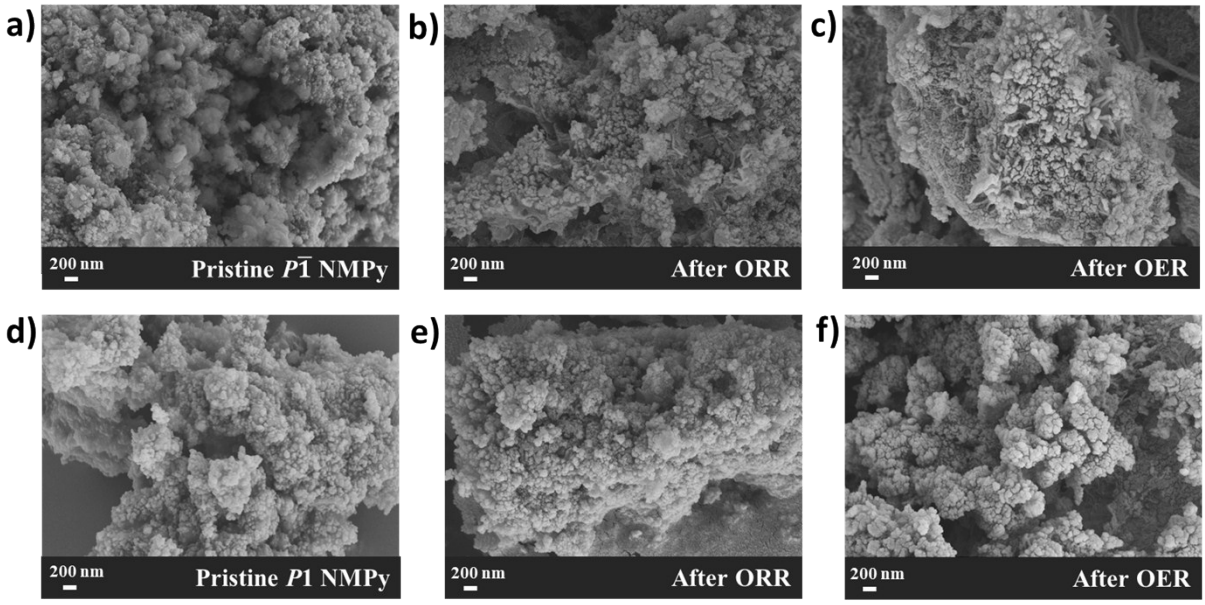

Figure S9. SEM image of (a) pristine NMPy-$P\bar{1}$ polymorph, (b) cycled NMPy-$P\bar{1}$ polymorph during ORR, (c) cycled NMPy-$P\bar{1}$ polymorph during OER, (d) pristine NMPy-$P1$ polymorph, (e) cycled NMPy-$P1$ polymorph during ORR, and (f) cycled NMPy-$P1$ polymorph during OER. All experiment of electrocatalysts were done in 0.1 M KOH.

Table S1. The calculated lattice parameters of $Na_2MnP_2O_7$ ($P\bar{1}$ NMPy) polymorph synthesized at 555℃.

Crystal System			Triclinic			Reliability factors	
Space group			$P\bar{1}$ (#2)				
Unit cell Parameters						Rf(%)	1.41
a	5.309(9)	b	6.584(9)	c	9.414(0)	Rwp(%)	2.09
∝	109.70(4)	β	95.14(2)	γ	106.31(8)	χ^2	6.52
						GoF-index	2.60
Unit cell volume(Å^3) [Z=2]					291.150(0)		

Wyckoff positions							
Atom	Atom type	site	x/a	y/b	z/c	B_{iso}(Å^2)	Occupancy
Na1	Na+1	2i	0.650(71)	0.869(33)	0.269(48)	0.007(00)	1
Na2	Na+2	2i	0.120(17)	0.771(86)	0.033(42)	0.078(00)	1
Mn1	Mn2+	2i	0.087(98)	0.598(02)	0.362(08)	0.009(00)	0.987(99)
P1	P5+	2i	0.258(14)	0.158(30)	0.386(19)	0.008(00)	0.987(06)
P2	P5+	2i	0.424(33)	0.320(85)	0.125(52)	0.061(65)	1
O1	O2-	2i	0.064(47)	0.301(30)	0.419(41)	0.076(35)	0.965(84)
O2	O2-	2i	0.493(26)	0.243(19)	0.521(76)	0.070(00)	1
O3	O2-	2i	0.103(62)	-0.086(02)	0.327(02)	1.622(39)	0.979(15)
O4	O2-	2i	0.381(81)	0.180(52)	0.231(72)	0.060(00)	0.971(24)
O5	O2-	2i	0.256(30)	0.478(35)	0.157(38)	0.063(34)	0.981(68)
O6	O2-	2i	0.320(34)	0.134(98)	-0.034(78)	0.732(17)	0.999(28)
O7	O2-	2i	0.720(29)	0.439(25)	0.165(00)	1.231(21)	1.043(27)

Table S2. The calculated lattice parameters of $Na_2MnP_2O_7$ ($P1$ NMPy) polymorph synthesized at 700 ℃.

Crystal System					Triclinic	Reliability factors	
Space group					$P1$(#1)		
Unit cell Parameters						Rf(%)	1.39
a	9.921(6)	b	11.088(4)	c	12.476(2)	Rwp(%)	1.95
∝	148.41(2)	β	121.95(2)	γ	68.42(2)	χ^2	4.92
						GoF-index	2.2
Unit cell volume(Å^3) [Z =4]					599.3022		

Wyckoff positions							
Atom	Atom type	site	x/a	y/b	z/c	B_{iso}(Å^2)	Occupancy
Na1	Na+1	1a	0.833(81)	0.112(76)	0.421(98)	1	1
Na2	Na+1	1a	0.140(08)	0.939(75)	0.589(02)	0.007(41)	1
Na3	Na+1	1a	0.877(39)	0.153(97)	0.065(64)	0.502(66)	1
Na4	Na+1	1a	0.139(38)	0.766(42)	0.916(68)	1	1

Na5	Na+1	1a	0.171(47)	0.694(19)	0.155(01)	1	1
Na6	Na+1	1a	0.820(21)	0.333(39)	0.867(04)	1	1
Na7	Na+1	1a	0.526(20)	-0.035(14)	-0.042(55)	2.651(79)	0.971(99)
Na8	Na+1	1a	0.470(56)	0.270(29)	0.330(41)	1	1
Mn1	Mn2+	1a	0.478(51)	0.419(07)	0.139(01)	1	
Mn2	Mn2+	1a	0.903(06)	0.857(60)	0.642(87)	1	0.998(81)
Mn3	Mn2+	1a	0.506(56)	0.598(12)	0.864(52)	1	1
Mn4	Mn2+	1a	0.103(01)	0.190(04)	0.390(08)	1	1
P1	P5+	1a	0.181(77)	0.353(43)	0.135(92)	1	1
P2	P5+	1a	0.730(12)	0.748(41)	0.292(33)	1	1
P3	P5+	1a	0.219(90)	0.543(12)	0.522(04)	1	1
P4	P5+	1a	0.476(10)	-0.008(01)	0.318(79)	1	1
P5	P5+	1a	0.843(19)	0.686(10)	0.916(04)	1.963(96)	1
P6	P5+	1a	0.286(27)	0.255(42)	0.700(55)	0.339(08)	0.996(28)
P7	P5+	1a	0.798(52)	0.476(09)	0.509(01)	0.637(52)	1
P8	P5+	1a	0.551(95)	-0.025(61)	0.663(15)	0.943(32)	1
O1	O2-	1a	0.301(94)	0.426(08)	0.365(16)	13.983(41)	1
O2	O2-	1a	0.313(32)	0.668(41)	0.721(63)	1	1
O3	O2-	1a	0.091(81)	0.411(98)	0.354(38)	3.416(77)	1
O4	O2-	1a	0.083(16)	0.669(13)	0.518(94)	0.385(93)	1
O5	O2-	1a	0.312(12)	0.199(62)	0.020(11)	1	1
O6	O2-	1a	0.060(73)	0.547(64)	0.160(73)	3.257(57)	1
O7	O2-	1a	0.075(04)	0.167(97)	-0.011(50)	3.554(43)	1
O8	O2-	1a	0.554(57)	0.778(09)	0.241(43)	1	1
O9	O2-	1a	0.719(74)	0.577(15)	0.259(82)	1	1
O10	O2-	1a	0.901(87)	1.035(55)	0.588(79)	1	1
O11	O2-	1a	0.730(27)	0.582(10)	0.073(52)	4.070(30)	1
O12	O2-	1a	0.477(86)	0.903(68)	0.121(09)	4.668(38)	1
O13	O2-	1a	0.237(62)	0.941(18)	0.208(46)	1	1
O14	O2-	1a	0.557(17)	0.257(60)	0.547(58)	1.106(28)	1
O15	O2-	1a	0.736(17)	0.555(89)	0.655(18)	1	1
O16	O2-	1a	0.666(56)	0.369(21)	0.313(51)	1	1
O17	O2-	1a	0.938(40)	0.357(54)	0.537(66)	0.793(33)	1
O18	O2-	1a	0.900(48)	0.719(38)	0.682(93)	1.278(95)	1
O19	O2-	1a	0.694(94)	0.796(68)	0.996(60)	1.763(64)	1
O20	O2-	1a	0.849(07)	0.453(77)	0.782(92)	1	1
O21	O2-	1a	0.928(81)	0.929(97)	0.060(39)	1.615(48)	1
O22	O2-	1a	0.446(14)	0.150(05)	0.670(60)	0.179(95)	1
O23	O2-	1a	0.140(69)	0.031(21)	0.466(98)	1	1
O24	O2-	1a	0.279(09)	0.375(07)	0.8938(2)	2.734(86)	1
O25	O2-	1a	0.331(71)	0.409(70)	0.740(30)	4.459(09)	1
O26	O2-	1a	0.719(21)	0.063(71)	0.755(41)	1	1
O27	O2-	1a	0.503(47)	0.054(42)	0.824(45)	1	1
O28	O2-	1a	0.440(06)	0.743(76)	0.418(10)	0.768(51)	1

Table S3. Onset potential and current density of $Na_2MnP_2O_7$ polymorphs for ORR and OER activity, which is compared with the Vulcan C and RuO_2 in 0.1 M KOH.

Polymorphs	ORR onset (V vs RHE)	Current Density (mA/cm^2) at 0.7 V	OER over-potential (V vs RHE)	Current Density (mA/cm^2) at 1.65 V
Vulcan C	0.89	2.9	----	----
RuO_2	----	----	0.285	9
$P\bar{1}$ NMPy	0.87	4	0.334	16
$P1$ NMPy	0.87	3	0.349	5

References:

1. J. Rodriguez-Carvajal, *Phys. B.*, 1993, **192**, 55.
2. T. Roisnel and J. Rodriguez-Carvajal, *Proc. 7th Eur. Powder Diff. Conf.*, 2000, 118.
3. K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 2008, **41**, 653.
4. http://www.casaxps.com/